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RUBBER CHEMISTRY AND TECHNOLOGY

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DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

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UNITED CARBON BLACKS have been recognized for their dependability and general excellence for more than three decades.

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A — **Philblack A, Fast Extrusion Furnace Black.** Excellent tubing, molding, calendering, finish! Mixes easily. Disperses heat. Non-staining.

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Polysar S-X371
Polysar Kryflex 200
Polysar Kryflex 252
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Polysar Butyl 200
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Polysar Butyl 402

LATICES

Polysar Latex II
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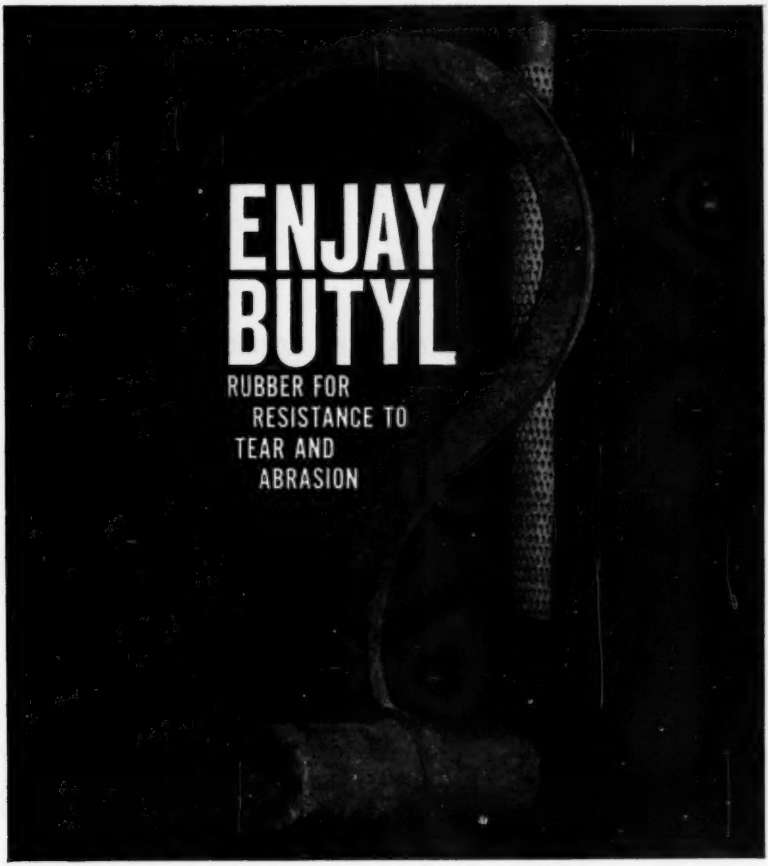

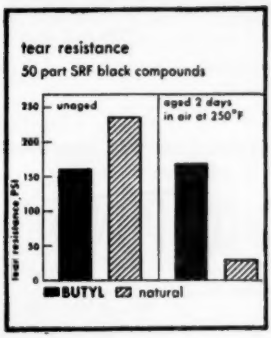

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Rubber Blue GD
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Hylene* M-50
Hylene* MP
Hylene* T
Hylene* TM
Hylene* TM-65

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RPA No. 3 Concentrated
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RR-10

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Plioflex, Wing-Stay, Pliolite, Chemigum—T. M.'s
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Write, on your letterhead, for technical data or assistance with any Naugatuck product.

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Division of United States Rubber Company
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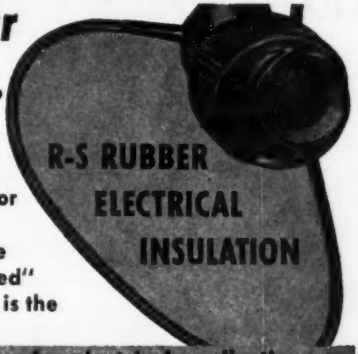

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COLD TYPES

GRADE	CLASS	END USES
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Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut

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This carboxyl-modified nitrile rubber gives a compound far more abrasion resistance than any other rubber. During laboratory testing, garnet paper actually wears out without making any headway against this Hycar rubber.

Hycar 1072 gives all the advantages of isocyanate rubber at considerably lower cost, besides providing easier processing. In addition, Hycar 1072 will provide high gum strength, good hot tensile and tear strength, and good oil resistance combined with resistance to ozone.

Hycar 1072 offers new opportunities for makers of caster wheels, skate wheels, hard rolls, loom parts, football shoe calks and shoe heels.

For further information about Hycar 1072, or information about any of the many other Hycar nitrile rubbers or latices, write Dept. CD-2, B.F.Goodrich Chemical Company, 3135 Euclid Avenue, Cleveland 15, Ohio. Cable address: Goodchemco. In Canada: Kitchener, Ontario.

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Rubber and Latex
B.F.Goodrich Chemical Company
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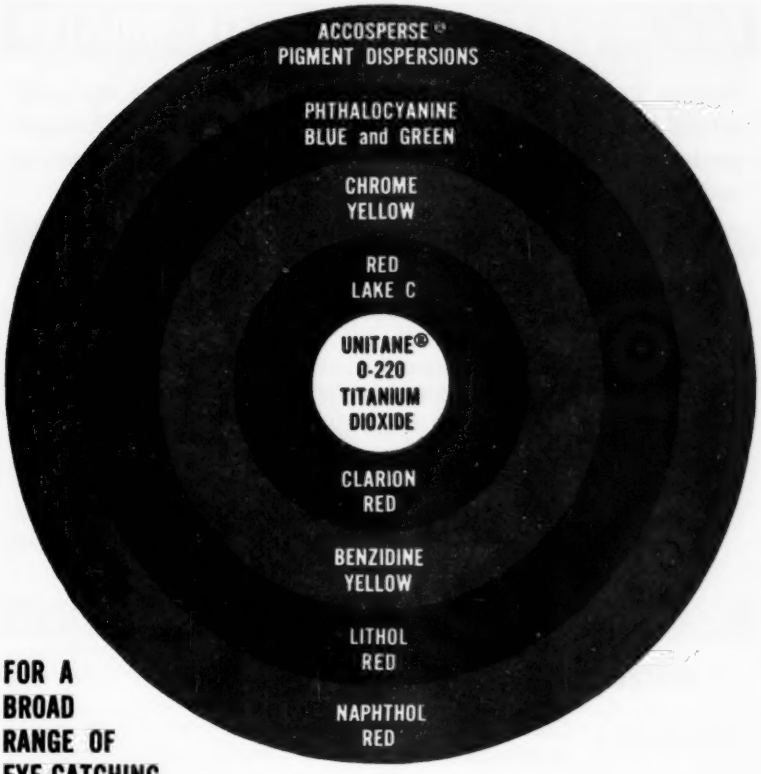

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General Tire's Chemical Division is constantly aware of the needs of the rubber industry, and provides these specially-formulated products to meet those needs. Write or call for further information and generous samples.

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GEN-TAC • Vinyl pyridine latex. Assures excellent fabric-to-rubber adhesion using nylon or rayon cords.

KO-BLEND • Latex-compounded masterbatch, 85% insoluble sulfur colloidally dispersed in GRS latex. Cuts whitewall rejects and reworks . . . eliminates spots, streaks and batch softening.

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RUBBER:

GENTRO • Top-quality cold SBR Polymers.

GENTRO-JET • Cold and oil-extended black masterbatches, for easier processing and more efficient production.

LATICES:

GEN-FLO • Styrene-butadiene, with balanced stabilization system, low odor, and excellent mechanical stability.

ACRI-FLO • Styrene-acrylic, offering excellent adhesion, mechanical stability and UV heat and light stability.

PVC RESINS:

VYGEN • a complete family of top-quality, versatile resins formulated to meet specific needs.

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CHEMICAL DIVISION • AKRON, OHIO

Creating Progress Through Chemistry

Chemical Division GENERAL
THE GENERAL TIRE & RUBBER CO.

Made by the originators of custom-blended Sunoco gasolines . . .

Sunoco's "Custom-Made" Process Oils Ease Problems of Quality Control

IF YOU PROCESS	USE	BECAUSE
Light-colored oil-extended polymers (1703, 1708, etc.)	CIRCOSOL® NS	It combines superior nonstaining characteristics with best processibility, imparts good physicals. Primarily an extender.
Oil-extended polymers (1703, 1708, etc.)	CIRCOSOL 2XH	It's a general-purpose softener and extender for light-colored rubber goods, especially where optimum physicals are required.
Regular neoprenes, natural rubber, SBR polymers, Hypalon (where color is a problem)	CIRCO® LIGHT	It's an ideal all-around moderate-priced plasticizer for nonstaining reclaims and butyl inner tubes, SBR, GN, W, WRT.
Oil-extended polymers (1705, 1710, etc.) and natural rubber, Hypalon (where color is no problem)	SUNDEX® 53	It's a double-distilled aromatic plasticizer for tire-tread stock, rubber footwear, matting, toys, semi-hard rubbers, high-Mooney WHV.
Black masterbatch polymers 1706, 1711, 1712, etc.	SUNDEX 1585	It's a new highly aromatic plasticizer for tough polymers where easy processing is desired. This is a distilled process aid.
Natural rubber, SBR polymers, regular and WHV neoprenes, acrylonitrile polymers	SUNDEX 85	It's especially recommended for very high loadings of WHV neoprene (from 75 to over 100 parts Sundex 85 to 100 parts polymer). Used in hard rubber goods.

Other Sun compounding oils, not listed, include a series of paraffin oil with low aromatic content; naphthenic oils with moderate aromatic content; and Sundex oils with high aromatic content. Sun's brochure: "A GRAPHIC METHOD FOR SELECTING OILS USED IN COMPOUNDING AND EXTENDING BUTADIENE-STYRENE RUBBERS" can help you select the best oil for your needs. Get a copy from your Sun man or write Dept. RC-10.

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Philprene* offers a tremendous variety!

CURRENT PHILPRENE POLYMERS		
	NON-PIGMENTED	PIGMENTED WITH PHILBLACK*
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COLD	PHILPRENE 1500 PHILPRENE 1502 PHILPRENE 1503	PHILPRENE 1601 PHILPRENE 1603** PHILPRENE 1605 **Pigmented with EPC Black
COLD OIL	PHILPRENE 1703 PHILPRENE 1708 PHILPRENE 1712	PHILPRENE 1803 PHILPRENE 6608 PHILPRENE 1805 PHILPRENE 6620 PHILPRENE 6604 PHILPRENE 6661*** PHILPRENE 6682*** ***Carbon black slurry made by Philjet* Process

There are non-staining Philprene rubbers for white-wall tires, appliance door gaskets and window seals. Light colored Philprenes for surgical goods and shoe soles. Also Philprene rubbers with tremendous abrasion resistance and long flex life . . . special Philprene polymers for the wire and cable industry . . . for nearly *everything* that's made of rubber!

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COLUMBIA-SOUTHERN CALCENE® PIGMENTS

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CALCENE® TM	CALCENE® NC	CALCENE® CO
(Original product) Surface-coated for fast and thorough dispersion.	(Non-Coated) Better in color than TM, but slightly harder dispersing.	(Coated) Clean white to provide true color values in finished goods.

Calcene may provide your rubber products with additional advantages required for better looks, better wear, better price. Use Calcene for pastel or colored goods . . . for improved hot tear resistance . . . for an equivalent high level of uniform physicals at greater economy compared with more costly ultra-fine carbonates. Local stocks provide fast service in Boston, Hoboken, Chicago and Los Angeles. Why not investigate Calcene right now? Price information and formulation suggestions may be obtained by contacting your nearest Columbia-Southern office or by writing Room 1929, One Gateway Center, Pittsburgh 22, Pennsylvania.

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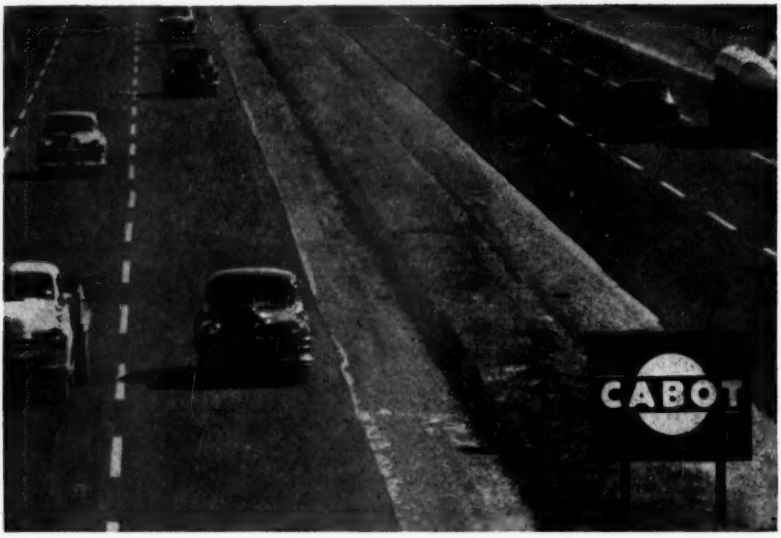


On the Road with

CABOT BLACKS

ON THE ROAD TESTS are an important part of the Cabot testing program . . . designed to provide the best reinforcing carbon blacks available. In addition to laboratory and factory tests, Cabot blacks are compounded in various types of rubber, and tires are subjected to miles and miles of grueling road tests. That's why Cabot blacks give consistently longer wear and trouble-free performance in all types of rubber. Complete production quality control further assures the same excellence of performance from every shipment of Cabot blacks.

CHANNEL BLACKS:	Spheron 9 EPC	Spheron 6 MPC		
FURNACE BLACKS:	Vulcan 9 SAF	Vulcan 6 ISAF	Vulcan 3 HAF	Vulcan XC-72 ECF
Vulcan SC SCF	Vulcan C CF	Sterling 99 FF	Sterling SO FEF	Sterling V GPF
Sterling L HMF	Sterling LL HMF	Sterling S SRF	Sterling NS SRF	Pelletex SRF
Pelletex NS SRF	Sterling R SRF	Gastex SRF		
THERMAL BLACKS:	Sterling FT	Sterling MT	Sterling MT-NS	
	Sterling FT-FF	Sterling MT-FF	Sterling MT-NS-FF	

Free Samples, Technical Literature Available

CABOT

GODFREY L. CABOT, INC.

125 HIGH STREET, BOSTON 10, MASSACHUSETTS

MONSANTO RUBBER CHEMICALS ANSWER ANOTHER IMPORTANT COMPOUNDING QUESTION

QUESTION: *What economical vulcanizing agent can give my stocks highest heat resistance and more safety from scorch with no bloom or discoloration?*

ANSWER: *SULFASAN R dithioamine vulcanizing agent*

You can get the best heat resistance at a reasonable cost *and* eliminate bloom in your finished compounds by partial replacement of conventional curing agents with SULFASAN R. At the same time, this unique vulcanizing agent provides greater safety from scorch and can also boost modulus, lower compression set and improve aging.

Economical SULFASAN R trims the cost of some compounds by reducing the total amount of vulcanizing agent required. As little as 0.8 to 2 parts of SULFASAN R per hundred of rubber, plus a small amount of THIURAD (tetramethylthiuram disulfide) or a similar curing agent, is usually sufficient to achieve good results in GR-S, butyl, nitrile and natural rubbers. For more information, use the convenient coupon.

	HEAT RESISTANCE	
COMPOUNDS	**A**	**B**
Nitrile Rubber	100	100
Zinc Oxide	5	5
Stearic Acid	1	1
FEF Black	40	40
THIURAD	3.50	0.80
SULFASAN R	—	0.80
CURING AGENT COST	$3.99	$2.15
RESULTS		
Mooney Scorch (Mins.), Large Rotor @ 250° F.	12.5	31
Compression Set 70 Hrs./100° C.	27%	24%
Blooming	1 day	None in 9 months
Unaged		
Tensile, psi	2480	2520
Elongation, %	530	500
Hardness	64	65
Aged 70 Hrs./300° F.		
Tensile, psi	600	780
Elongation, %	20	30
Hardness	85	87

See how a lower-cost SULFASAN R/THIURAD system compares with THIURAD alone in a heat-resistant nitrile rubber compound.

LET MONSANTO RUBBER CHEMICALS ANSWER YOUR NEXT COMPOUNDING QUESTION

Jot it down on your letterhead. No obligation—no salesman will call (unless you so request). To help you solve specific problems, Monsanto draws from basic knowledge of more than 85 rubber chemicals and over 18,000 compounding studies. Write, today.

SULFASAN, THIURAD: Monsanto T. M.'s, Reg. U. S. Pat. Off.

Monsanto Chemical Company
Rubber Chemicals Department
Akron 11, Ohio

☐ Please send me more information about SULFASAN R

*Name*_____ *Title*_____

*Company*_____

*Address*_____

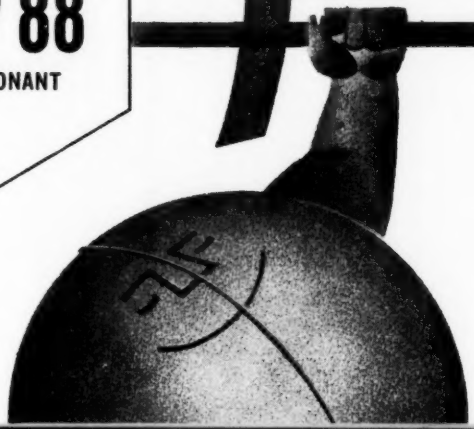
*City*_____ *Zone*____ *State*_____

Monsanto ®

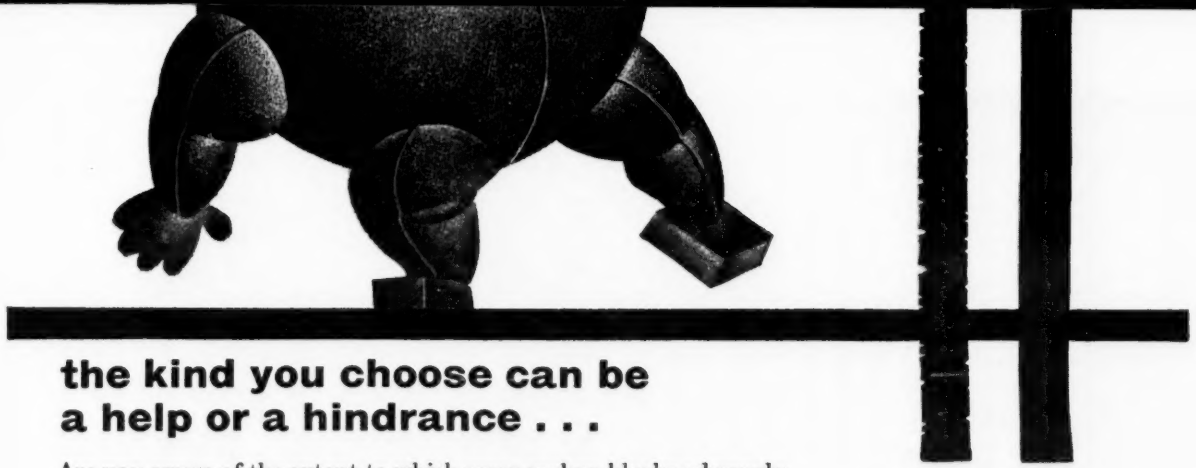
what type of CARBON BLACK helps fight ozone attack?

UOP 88®
ANTIOZONANT

UOP 288®
ANTIOZONANT



The SBR specimens below were exposed to ozone at 100° F, 20 percent elongation, 52 hr. at 33 pphm ozone, then 187 hr. at 63 pphm ozone.



the kind you choose can be a help or a hindrance . . .

Are you aware of the extent to which some carbon blacks adversely affect the protection afforded rubber products by antiozonants?

Some inactivate much of the antiozonant added for ozone protection. Others are more compatible with the antiozonant.

The two rubber test strips shown at right are clear evidence that carbon black plays an extremely important part in obtaining maximum service life of rubber compounded with antiozonants.

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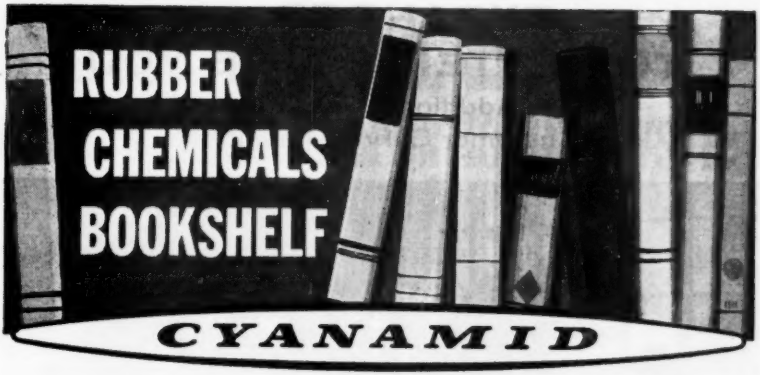

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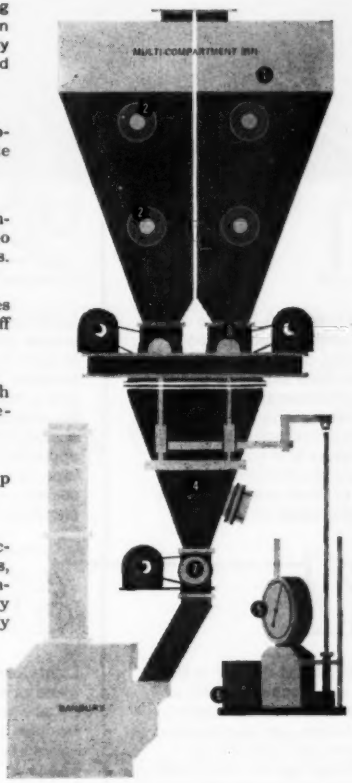

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1960	Fall	New York	Commodore	Aug 28–Sept 3
1961	Spring	Louisville	Brown	April 18–21
1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	May 15–18
1962	Fall	Philadelphia	—	September 11–14
1963	Spring	Toronto	Royal York	May 7–10
1963	Fall	New York	Commodore	September 10–13
1964	Spring	Detroit	Cadillac	April 28–May 1
1964	Fall	Chicago	Sherman	September 1–4

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Buffalo Rubber Group

Chairman: Richard Herdlein (Hewitt-Robins, Inc., Buffalo). *Vice-Chairman:* Larry Halpin (Dunlop Tire & Rubber Co., Buffalo). *Secretary-Treasurer:* Ed Sverdrup (U. S. Rubber Reclaiming). *Asst. Sec'y-Treasurer:* Donald E. Jones (U. S. Rubber Reclaiming Co.) *Directors:* Jack Wilson (Dow Corning), Jack Haller, Eugene Martin (Dunlop Tire & Rubber Co.), Robert Donner (National Aniline), Robert Prior (Hewitt-Robins, Inc.), Ed Haas (Dunlop Tire and Rubber Corp.). Meeting dates in 1959: May 1—(International Rubber Group Meeting, General Brock Hotel, Niagara Falls, Canada, June 9, October 13, December 8.

Chicago Rubber Group

President: John Groot (Dryden Rubber Division, Sheller Mfg. Company, 1014 South Kildare Avenue, Chicago 24, Illinois). *Vice-President*: Stanley F. Cholte (Tumpeer Chemical Company, 333 North Michigan Avenue, Chicago 1, Illinois). *Secretary*: T. C. Argue (Roth Rubber Company, 1860 South 54th Street, Cicero, Illinois). *Treasurer:* R. A. Kurtz (E. I. du Pont de Nemours & Co., Inc., 75 Dearborn Street, Chicago, Illinois). *Directors:* H. E. Minnerly Jr. (B. F. Goodrich Company), Stanley Shaw (Witco Chemical Company), J. C. Toman (Victor Mfg. & Gasket), Richard Huhn (Harwick Standard Chemical Co.), Cornelius Woods (Dryden Rubber Division), Joseph Ross (O'Connor & Company), Frank E. Smith (Williams-Bowman Rubber Co.), Irwin Najdl (Ideal Roller & Mfg. Company). Meetings Dates: September 18, 1959, November 6, 1959, January 29, 1960, March 11, 1960, April 22, 1960.

The Connecticut Rubber Group

Chairman: W. H. Couch (Whitney Blake Co., Hamden, Conn). *Vice-Chairman:* V. P. Chadwick (Armstrong Rubber Co., West Haven, Conn.).

Secretary: A. MURDOCK (Armstrong Rubber Co., West Haven, Conn.). *Treasurer:* F. B. SMITH (Naugatuck Chem. Div., Naugatuck, Conn.). Meetings in 1959: February 21, May 22, September 12, November 6.

DETROIT RUBBER GROUP

Chairman: W. F. MILLER (Yale Rubber & Mfg. Co., Sandusky, Michigan). *Vice-Chairman:* W. D. WILSON (R. T. Vanderbilt Co., Detroit). *Secretary-Treasurer:* P. V. MILLARD (Automotive Rubber Co., Detroit). *Directors:* J. F. STIFF, J. M. CLARK, JACK MASDEN, A. F. THOMPSON, FRANK G. FALVEY, R. W. MALCOLMSON, C. H. ALBERS, R. HUIZINGA, E. P. FRANCIS, J. J. FLEMING, R. C. CHILTON, S. M. SIDWELL, R. H. SNYDER, R. C. WATERS, E. W. TILLITSON, T. W. HALLORAN. *Councilors:* H. F. JACOBER, H. W. HOERAUF, J. T. O'REILLY. Meetings in 1959: April 18, June 26, October 2, December 2.

FORT WAYNE RUBBER GROUP

Chairman: WALTON D. WILSON (R. T. Vanderbilt Co., 5272 Doherty Dr., Orchard Lake, Michigan). *Vice-Chairman:* A. BLUESTEIN (Anaconda Wire & Cable Co., Marion, Ind.) *Secretary-Treasurer:* A. L. ROBINSON. *Directors:* M. J. O'CONNOR, NORMAN KLEMP, E. THEALL, H. CANTWELL, H. GLASSFORD, J. LAWLESS, R. HARTMAN, S. CHOATE, E. BOSWORTH. Meetings in 1959: June 5 (outing), September 24.

LOS ANGELES RUBBER GROUP

Chairman: CHARLES H. KUHN (Master Processing Corp., Lynwood). *Assoc. Chairman:* B. R. SNYDER (R. T. Vanderbilt Co., Los Angeles). *Vice-Chairman:* W. M. ANDERSON. *Secretary:* C. M. CHURCHILL (Naugatuck Chemical, East Los Angeles). *Asst. Secretary:* EDMUND J. LYNCH (H. M. Royal, Inc., Downey, Calif.). *Treasurer:* HOWARD R. FISHER (W. J. Voit Rubber Co., Los Angeles). *Directors:* ROY N. PHELAN (Atlas Sponge Rubber Co., Monrovia), WILLIAM J. HANEY (Kirkhill Rubber Co., Brea), JOHN L. RYAN (Shell Chemical Corp, Torrance), CARL E. HUXLEY (Enjay Co., Los Angeles), WALTER E. BOSWELL (Thiokol Chemical Corp.). Meetings in 1959: May 5, June 5, 6 and 7, October 6, November 3, December 11.

NEW YORK RUBBER GROUP

Chairman: R. B. CARROLL (R. E. Carroll, Inc., Trenton, N. J.). *Vice-Chairman:* E. S. KERN (R. T. Vanderbilt, 230 Park Ave., N. Y.). *Secretary-Treasurer:* R. G. SEAMAN (Rubber World, New York). Terms end December 31, 1959. Meetings in 1959: October 16, December 18 at Henry Hudson Hotel.

NORTHERN CALIFORNIA RUBBER GROUP

President: DRACE "KUT" KUTNEWSKY (Burke Rubber Co., San Jose). *Vice-President:* CLAUDE "CORKY" CORKADEL (Oliver Tire & Rubber Co., Oakland). *Treasurer:* JOE MATTSON (Witco Chemical Co., San Francisco). *Secretary:* RAY BROWN (Burke Rubber Co., San Jose). *Directors:* KEITH LARGE, VIC CARRIERE. Meetings in 1959: September 5, October 8, November 5, December 5.

Philadelphia Rubber Group

Chairman: R. S. Graff (E. I. du Pont de Nemours & Co., Wilmington). *Vice-Chairman:* H. C. Remsberg (Carlisle Tire & Rubber, Carlilse, Pa.). *Secretary-Treasurer:* R. N. Hendrickson (Phillips Chemical Co., 2595 East State Street, Trenton, N. J.). *Executive Committee:* T. E. Farrell, R. N. Hendriksen, James Jones, George N. McNamara, J. R. Mills, H. M. Sellers, Merrill Smith. *National Dir.:* M. A. Youker (E. I. du Pont de Nemours & Co., Wilmington). Meetings in 1959: May 1, August 21, October 2 (Poor Richard Club), November 6 (Dance for members only).

Rhode Island Rubber Group

Chairman: H. W. Day (E. I. du Pont de Nemours & Co., Boston). *Vice-Chairman:* Harry L. Ebert (Firestone, Fall River, Mass.). *Secretary-Treasurer:* W. J. Blecharczyk. *Historian:* R. G. Bolkman (U. S. Rubber Co., Providence). *Executive Committee:* E. S. Uhlig, R. B. Robitaille, J. M. Vitale, C. A. Damicone, G. E. Enser. Meetings in 1959: June 12–14, November 5, Pawtucket Country Club, Pawtucket, R. I.

Southern Ohio Rubber Group

Chairman: R. J. Hoskin (Inland Mfg. Div., Dayton, Ohio). *Chairman-Elect:* F. W. Gage (Dayton Chem. Products Labs., West Alexandria, Ohio). *Treasurer:* J. M. Kelble (Wright Patterson AF Base, Ohio). *Secretary:* R. E. Wells (Precision Rubber Prod. Co., Dayton 17, Ohio). *National Director:* F. W. Gage (Dayton Chem. Products Labs., West Alexandria, Ohio). Meetings in 1959: October 8, December 12.

Southern Rubber Group

Chairman: Warren Hall (Phillips Chemical Co., 318 Water Street, Akron, Ohio). *Vice-Chairman:* E. H. Ruch (Firestone Tire and Rubber Co., Memphis, Tenn.). *Secretary:* E. Strube (E. I. du Pont de Nemours and Co., Atlanta, Ga.). *Treasurer:* R. C. Whitmore (Better Monkey Grip Co., Dallas, Texas). Meeting in 1959: Oct. 9 and 10 Peabody Hotel, Memphis, Tenn. Meeting in 1960: Feb. 12 and 13 Shamrock Hilton Hotel, Houston, Texas.

Washington Rubber Group

President: Robert Stiehler (National Bureau of Standards). *Vice-President:* A. W. Sloan (Atlantic Research, Alexandria, Va.). *Secretary:* George T. Richey (National Bureau of Standards). *Treasurer:* J. R. Britt (B. F. Goodrich Co.). *National Director:* A. W. Sloan. Meetings in 1959: April 6, May 4, Patomac Electric Power Co. Auditorium.

Ontario Rubber Group

Chairman: O. R. Huggenberger (Dominion Rubber Co. Ltd., Montreal).

75TH MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY,

MAY 13–14–15, 1959

BILTMORE HOTEL, LOS ANGELES, CALIFORNIA

TECHNICAL PROGRAM

E. H. KRISMANN, *Chairman;* ROSCOE H. GERKE, *Secretary*

WEDNESDAY—MAY 12

TECHNICAL SESSION A—SYMPOSIUM ON URETHANE FOAMS AND ELASTOMERS

Invited Papers

G. T. GMITTER, *Presiding*

1A. Introductory Remarks. E. H. Krismann, Chairman

2A. Urethane Polyether Prepolymers and Foams—Influence of Chemical and Physical Variables on Reaction Behavior. H. G. Scholten, *J. G. Schuhmann*, R. E. TenHoor, The Dow Chemical Company, Midland, Michigan

3A. Organo-Tin Compounds as Catalysts for Reactions of Isocyanates with Active Hydrogen Compounds. *F. Hostettler*, E. F. Cox, Union Carbide Chemicals Co., South Charleston, West Virginia

4A. Some Properties and Applications of Loaded Flexible Urethane Foams. *S. J. Assony*, S. Chess, Freedlander Research & Dev. Lab., American Latex Products Corp., Hawthorne, California

5A. The Mechanism of the Water Reaction with Isocyanates. G. Shkapenko, *G. T. Gmitter*, E. E. Gruber, The General Tire & Rubber Co., Central Research Laboratories, Akron 9, Ohio

6A. "Chemical Compounding" of Liquid Urethane Elastomers. *R. J. Athey*, Elastomers Laboratory, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

7A. The Development of Cast Urethane Elastomers for Ultimate Properties. K. A. Pigott, *B. F. Frye*, K. R. Allen, S. Steingiser, W. C. Darr, J. H. Saunders, E. E. Hardy, Research Department, Mobay Chemical Company, New Martinsville, West Virginia

TECHNICAL SESSION B—EFFECT OF OZONE ON RUBBER

Contributed Papers

W. J. SPARKS, *Presiding*

2B. Compounding Variables Affecting Antiozonant Requirements. *W. L. Cox*, Universal Oil Products Co., Des Plaines, Illinois

3B. The Ozone Resistance of Styrenebutadiene Rubber at Low Temperatures. *R. F. Grossman*, A. C. Bluestein, Anaconda Wire & Cable Co., Research Laboratories, Marion, Indiana

4B. A Method of Screening Antiozonants. *F. A. V. Sullivan*, A. R. Davis, American Cyanamid Company, Bound Brook, New Jersey

5B. Correlation of Ozone Chamber and Outdoor Exposure. *H. A. Winkelmann*, Dryden Rubber Division, Sheller Mfg. Corp., Chicago, Illinois

6B. Comparative Performance of Antiozonants in Road and Accelerated Tests in the Los Angeles Area. *F. B. Smith*, Naugatuck Chemical Division, United States Rubber Co., Naugatuck, Connecticut

7B. Resistance of Rubber Compounds to Outdoor and Accelerated Ozone Attack II. *G. N. Vacca*, G. H. Bebbington, R. E. Johnson, Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

8B. Wingstay 100 as an Antiozonant. J. C. Ambelang, *B. W. Habeck*, The Goodyear Tire & Rubber Co., Akron 16, Ohio

9B. Accelerated Aging Tests and Outdoor Performance of Butyl Rubber. *D. R. Hammel*, W. W. Gleason, Enjay Laboratories, Linden, New Jersey

THURSDAY—MAY 13

TECHNICAL SESSION—SYMPOSIUM ON EFFECT OF OZONE ON RUBBER

Invited Papers

H. A. WINKELMANN, *Presiding*

10. Operation of Ozone Chambers in Rubber Laboratories to Minimize Variation in Test Results. *M. Lowman*, The Goodyear Tire & Rubber Co., St. Marys Plant, St. Marys, Ohio

11. Ozone Resistance of Rubber Insulations. W. H. Couch, *G. H. Hunt*, O. S. Pratt, Simplex Wire & Cable Co., 79 Sidney Street, Cambridge, 39, Massachusetts

12. Weather Aging of Elastomers on Military Vehicles. *W. D. England*, J. A. Krimian, R. H. Heinrich, Ordnance Tank Automotive Command, Detroit Arsenal, Center Line, Michigan

13. Chemical Inhibition of Ozone Degradation of SB-R. *H. W. Kilbourne*, G. R. Wilder, J. E. VanVerth, J. O. Harris, Organic Chemicals Division, Monsanto Chemical Company, Nitro, West Virginia

Business Meeting

14. Ozone Cracking of Rubber in the Los Angeles Area. A. J. Haagen-Smit, M. F. Brunelle, *J. W. Haagen-Smit*, Division of Biology, California Institute of Tech., Pasadena, California

15. Factors Influencing the Ozone Resistance of Neoprene Vulcanizates under Flexure. *R. M. Murray*, Elastomers Lab., E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

Plant Trips

Rubber Division Banquet, Beverly Hilton Hotel

FRIDAY—MAY 14

TECHNICAL SESSION A—GENERAL PAPERS ON RUBBERS, ETC.

Contributed Papers

B. R. SNYDER, *Presiding*

16A. The Chelating Agent in Sulfoxylate Polymerization. R. D. Spitz, *A. K. Prince*, Technical Service & Dev. Lab., The Dow Chemical Company, Midland, Michigan

17A. Preparation and Physical Properties of Mixtures of Butadiene-Acrylic Acid and Butadiene-Vinylpyridine Elastomers. *C. A. Uraneck*, R. J. Sonnenfeld, Phillips Petroleum Company, Research & Development Dept., Bartlesville, Oklahoma

18A. Constitution and Variability of Rubber from Individual Trees. *A. R. Kemp*, Rubber Technology Foundation, Univ. of Southern California, Los Angeles 7, California

19A. Butyl Rubber Latex—A Review of Its General Properties in Non-transport Applications. A. L. Miller, *K. W. Powers*, Esso Research & Engineering Co., Linden, New Jersey

20A. Gel Formation in Styrene-Butadiene Rubbers. *C. A. Carlton*, J. M. Huber Corporation, Borger, Texas

21A. Terpolymer Rubbers: Standardization of Infrared Analysis by Chemical and Radiotracer Methods. *G. B. Sterling*, J. G. Cobler, D. S. Erley, F. A. Blanchard, The Dow Chemical Company, Midland, Michigan

22A. A High Temperature, Fluid Resistant Fluorocarbon Elastomer. *D. A. Stivers*, F. J. Honn, Minnesota Mining & Mfg. Co., St. Paul, Minnesota

23A. Fibrous Silicone Rubber. *R. A. Russell*, The Connecticut Hard Rubber Co., New Haven 9, Connecticut

24A. A Study of Abrasion and Road Wear of Butyl Tires Through Designed Compounding Experiments. *C. W. Umland* II, R. L. Zapp, Enjay Laboratories, Linden, New Jersey, and L. R. Sperberg, 3-T Fleet Inc., Odessa, Texas

TECHNICAL SESSION B—GENERAL PAPERS ON VULCANIZATION, ETC.

Contributed Papers

A. W. HAWKINS, *Presiding*

16B. Room Temperature Sulfur and Nonsulfur Vulcanization of Natural Rubber I. with Sulfur and Piperidinium N-Pentamethylene-Dithiocarbamate. II. With Quinone Dioxime (GMF) and Yellow Mercuric Oxide. *H. L. Fisher;* Univ. of Southern California, Los Angeles 7, California

17B. Vulcanization with TMTD. *E. M. Bevilacqua,* Research Center, United States Rubber Co., Wayne, New Jersey

18B. Sulfur Donor Vulcanization Systems Yield Improved Butyl Rubber Vulcanizates. *C. J. Jankowski,* K. W. Powers, R. L. Zapp, Enjay Laboratories, Linden, New Jersey

19B. Cardolite® Brand NX-3256 and NX-3216 Resins for Curing Butyl Rubber for Heat Resistant Applications. F. A. Moller, *D. A. Stivers,* Minnesota Mining & Mfg. Co., St. Paul, Minnesota

20B. Chemical-Loaded Molecular Sieves as Latent Curing Aids. III. A New Resin Curing System for Butyl Rubber. *F. M. O'Connor,* R. L. Ways, Molecular Sieve Products, Linde Company, Div. of Union Carbide Corp., Tonawanda, New York

21B. The Influence of the Order of Addition of Compounding Ingredients on Stocks Milled at Elevated Temperatures. *H. C. Jones,* New Jersey Zinc Co., Research Dept., Palmerton, Pennsylvania

22B. Mold Lag in Laboratory Rubber Sheet (Modulus) and Rebound Block Curing. *H. A. Freeman,* S. D. Gehman, The Goodyear Tire & Rubber Co., Akron 16, Ohio

23B. Development of Rubber Based Insulation Materials for Solid Rocket Motors. *O. D. Ratliff,* H. J. McSpadden, Astrodyne Inc., McGregor, Texas

24B. The Structure of Carbon Blacks. *A. Voet,* W. N. Whitten, Jr., J. M. Huber Corporation, Borger, Texas

Note: Deadline for papers for the Buffalo Meeting is March 10, 1960. Send seven copies of abstract to R. H. Gerke, Secretary.

ELECTION OF CHARLES GOODYEAR MEDALIST

Fernley H. Banbury, retired from Farrel-Birmingham Company, was elected as Charles Goodyear Medalist. He was overjoyed and accepted with many thanks.

SULFUR GROUP ANALYSES IN NATURAL RUBBER VULCANIZATES *

MERTON L. STUDEBAKER AND LESTER G. NABORS

PHILLIPS CHEMICAL COMPANY, AKRON, OHIO

Uncertainty as to the nature of the crosslinks in vulcanized rubber has been a tremendous handicap to chemical studies of vulcanization. A direct result is that physical methods have been the most successful in providing definite information about the nature of vulcanized rubber. However, these physical methods also possess serious limitations. A brief review may be in order on the methods which have provided insight into the chemical nature of the crosslinks.

A tremendous amount of information has been obtained on the reactions between sulfur and various olefins at vulcanizing temperatures. Much, but not all, of this work has been carried out in the laboratories of the British Rubber Producers' Research Association[1]. These studies are too extensive to review in detail here. But some of the impressions gained from studying them are: (1) There is no evidence that reaction with sulfur produces any carbon-to-carbon bonds. (2) The linkages produced between different molecules (intermolecular) are monosulfides, disulfides and polysulfides. The dominant linkage and the amount of polysulfide sulfur depends on the nature of the olefin, the reaction conditions and the presence of auxiliary materials such as accelerators, zinc oxide and fatty acids. (3) In the initial stages of the reaction, more polysulfide groups are present than in the later stages. Some of the sulfur in these polysulfide groups appears to react with the rubber to form five- and/or six-membered rings, and is referred to as "cyclic sulfur". The intermolecular sulfur-containing groups which survive contain less sulfur on the average than those present during the early part of the reaction.

Various sulfur-containing vulcanizates have been treated with methyl iodide to obtain information on the nature of the crosslinks. Selker and Kemp, in particular, reported extensive studies on a variety of model compounds and on rubber vulcanizates[2]. Methyl iodide reacts readily with diallyl monosulfides, forming trimethyl sulfonium iodide which can be removed by acetone extraction. Under the conditions specified by Selker and Kemp, the loss of sulfur is an indication of the amount of diallyl monosulfides. However, the results are not easy to interpret; some basic experimental work remains to be done, as indicated by Selker[2c]. When treated with methyl iodide, two of Selker's and Kemp's compounds lost more sulfur than the others: (a) a pale crepe-TMTD "sulfurless" cure and (b) a pale crepe-sulfur cure, accelerated with MBT, which was vulcanized at 134.5° C *for 17 hours*. Shorter cures of this latter compound lost much less sulfur during the treatment. Moore[3] has utilized methyl iodide to degrade natural rubber-TMTD "sulfurless" cures. Crosslinks were determined before and after a series of treatments, most of which were much more severe than those employed by Selker and Kemp for allyl monosulfides. Complete degradation was not possible, but approximately 85% of the crosslinks

* An original contribution.

were destroyed. The conclusion for this work is that the crosslinks contain sulfur.

Dogadkin and Tarasova[4] employed stress relaxation at various temperatures in an inert atmosphere to indicate bond types. Up to 70° C, all vulcanizates behaved in a similar manner. When stress relaxation was measured at successively higher temperatures or at a given high temperature (say 130° C), a considerable difference between various vulcanizates was observed. The order of resistance to stress relaxation was found to be: TMTD "sulfurless" cures, most resistant; MBT-accelerated sulfur cures, somewhat less; and DPG-accelerated cures, much less resistant. In fact, the DPG-accelerated cures were only slightly superior in this respect to unaccelerated sulfur vulcanizates. Dogadkin and Tarasova related this stress relaxation phenomenon to bond energies, reasoning that the higher bond energy of the C—S bond in monosulfides would require a higher temperature to rupture than the S—S bonds in disulfides or polysulfides. Polysulfide bonds should be less stable thermally than these other types. The presence of polysulfide bonds in DPG-accelerated sulfur cures and their absence in TMTD "sulfurless" cures were confirmed by prolonged treatment with 10% sodium sulfite. Subsequently, these findings were substantiated[5] by isotopic exchange of the polysulfide sulfur with S^{35}. The most serious limitations of the method are: (1) It is purely qualitative. (2) It cannot be applied to vulcanizates containing more than one type of bond, some other method being required to provide this information. (3) It is doubtful whether the method is sufficiently sensitive to differentiate between C—C and C—S—C bonds on the one hand and between disulfides and polysulfides on the other.

A number of attempts have been made to gain insight into the chemical nature of crosslinks by use of organically-combined sulfur—more recently in combination with crosslink measurements by equilibrium modulus or swelling. This procedure has so many limitations that it is virtually useless. Obviously, one would have to be able to determine what portion of the organically-combined sulfur was actually in the crosslinks before any useful calculations could be made. Even then, it would not be suitable if more than one type of crosslink were present. Perhaps the most successful use of this method is by Barton, who feels that, under conditions of maximum crosslinking efficiency (long curing time at low temperatures, low sulfur, high MBT, high zinc oxide and high stearic acid levels), the crosslinks in his particular MBT-accelerated vulcanizates are predominately monosulfidic[6].

Heretofore, the most useful tool which has been used to obtain information about the chemical nature of sulfur vulcanizates depends on isotope exchange[7] using S^{35}. The experimental basis of the method rests on the observation that sulfur in aliphatic mono- and disulfides (groups containing C—S linkages) will not exchange with labeled free sulfur, polysulfide sulfur or sulfur in sulfur-containing accelerators like MBT and TMTD. The exchange of combined sulfur of a vulcanizate is considered to be a definite indication that a part of this sulfur is in polysulfide bonds, e.g., attached only to other sulfur atoms as the S_x in R—S—S_x—S—R.

A number of investigations have been reported and a variety of techniques employed. Some of the important observations are:

(1) TMTD "sulfurless" cures contain no exchangeable (polysulfide, S_x) sulfur. The crosslinks are believed to be C—C, C—S—C or C—S—S—C groups[5b].

(2) DPG, MBT and TMTD, when used as accelerators for vulcanization by sulfur, produce crosslinks with exchangeable (polysulfide) sulfur. When used as an accelerator, DPG produces the largest amount of polysulfides, MBT somewhat less and TMTD the least, based on the total sulfur compounded in the stock[8].

(3) Polysulfides form in the early stages of accelerated vulcanization (or in unaccelerated vulcanization of hard rubber) and are converted during the later stages of cure to crosslinks containing less sulfur[9,10].

(4) The polysulfide crosslinks are less stable to heat than those which do not contain exchangeable sulfur. This is shown by the stress relaxation experiments referred to above.

Application of the method is seriously restricted by the lack of methods of determining the amount and nature of the other types of crosslinks likely to be present. Thus, it is impossible to determine whether all the crosslinks in a given vulcanizate are polysulfidic or only a part of them. Furthermore, existing methods do not enable one to determine the number of sulfur atoms in the polysulfide groups.

Based on the work reported in the literature, it seems reasonable to assume that in sulfur-cured and in TMTD "sulfurless"-cured gum stocks the crosslinks in vulcanizates are monosulfides, disulfides, polysulfides or mixtures of these groups. Carbon-to-carbon crosslinks have not been demonstrated in these vulcanizates, nor have they been indicated in any of the studies with model systems.

In the case of carbon black-loaded stocks, one might speculate that carbon-to-carbon bonds are produced between the carbon black particles and rubber molecules. Also, that they were produced during the formation of "bound rubber". However, if these C—C crosslinks are formed in natural rubber, they may well result in non-homogeneous crosslink distribution; and they are not measured—or, if measured, contribute very little to the "apparent crosslinks" measured by the swelling technique[11].

The work reported here is based on the reactions of lithium aluminum hydride with organic disulfides and polysulfides[12,13]. In essence, a disulfide molecule is converted by this reducing agent to two molecules of mercaptan; a polysulfide molecule, R—S—S_x—S—R, is converted to two molecules of mercaptan and x sulfide ions. Most monosulfides are not attacked by the reagent under the conditons which we employed. (A notable exception is diallyl monosulfide. See Table VI.)

$$(1)\quad \mathrm{R{-}S{-}S{-}R} \xrightarrow[\text{(and hydrolysis)}]{\mathrm{LiAlH_4}} 2\ \mathrm{RSH}$$

$$(2)\quad \mathrm{R{-}S{-}S_x{-}S{-}R} \xrightarrow[\text{(and hydrolysis)}]{\mathrm{LiAlH_4}} 2\ \mathrm{RSH} + x\mathrm{S}^{--}$$

If the total crosslinks can be determined by the swelling method, then the monosulfide crosslinks (or more specifically the sum of the crosslinks not attacked by the $LiAlH_4$) can be obtained by difference.

The method when applied to vulcanizates assumes:

(1) The crosslinks are monosulfide, disulfide or polysulfide bonds. Carbon-to-carbon crosslinks would be reported as monosulfide, and some other method would be required to determine their presence.

(2) Total crosslinks can be determined by calculation from swelling measurements in both gum and carbon black-loaded vulcanizates. The method detailed by Kraus[14] was used.

(3) The disulfide and polysulfide crosslinks react like similar bonds in smaller molecules.

(4) The sulfide and mercaptan of the reduced samples can be titrated potentiometrically even though the rubber is not in solution.

DEVELOPMENT OF THE PROCEDURE AND EXPERIMENTS WITH KNOWNS

In building the background information for the reductions with $LiAlH_4$, many experiments were run under a variety of conditions. These will not be reported in detail because they are not strictly comparable and because of their number.

In general, conditions could be found which would give good analyses for a variety of known disulfides and for di-tert-butyl trisulfide. However, the procedure for analyzing rubber samples was worked out to take care of a number of complications peculiar to this material. The reaction conditions are

TABLE I

EFFECT OF TEMPERATURE ON THE REDUCTION OF DIBENZYL DISULFIDE BY $LiAlH_4$

Temperature	Millimoles disulfide added	Millimoles found			% Recovery
		Sulfide	Mercaptan	Total	
175° C	0.2027	0.1826	0.0164	0.1990	98.2
150	0.2047	0.1645	0.0441	0.2086	101.9
100	0.2060	0.0619	0.1475	0.2094	101.0
65	0.2017	0.0112	0.1858	0.1970	97.7

probably too severe for any but the most stable di- and polysulfides. During the reduction of such materials, care must be taken to avoid converting the *mercaptan sulfur* to *sulfide*, a process which depends on time, temperature and possibly other conditions. As an example, dibenzyl disulfide was reduced for one hour at various temperatures by $LiAlH_4$ in Ansul ether No. 181. Although the recovery of sulfur was fairly quantitative, the amount of mercaptan found by titration decreased and the amount of sulfide sulfur increased with increasing temperature, Table I. The experiments were conducted at temperatures up to 270° C; but, above 175°, the mercaptan breaks were so indistinct as to be indefinite. Furthermore, the reagent decomposed at about 210° (hydrogen evolution).

Our early experiments with di-tert-butyl disulfide and di-tert-butyl trisulfide (pure samples obtained from the Research and Development Department of Phillips Petroleum Company) showed that these compounds were quantitatively reduced in accordance with Equations (1) and (2). The data in Table II were obtained by conducting the reduction at 65° C in boiling THF (tetrahydrofuran) for one hour. These were the first tests run on these materials.

The chief factors in the application of the procedure to vulcanizates were (1) the necessity of using rubber in a solid form even through the titration step, (2) the belief that the procedure which gave the highest mercaptan values would probably be preferable to any other and (3) the desirability of keeping the reaction conditions sufficiently mild as to avoid or minimize the conversion of

mercaptan to sulfide. Experiments at temperatures above 200° C showed that the vulcanizates could be degraded and handled in solution, but the mercaptan and sulfide values were quite erratic. It was found that thin sections or minute pieces of rubber were needed, since the quantities of sulfide and mercaptan increased as the particle size of the rubber samples was reduced. The mercaptan values were particularly dependent on this state of division. The most practical solution to this problem that we have found is to fracture the vulcanizate on a cold, tight rubber mill and then to inbed the weighed sample in paraffin and section to ca. 5 microns with a motor-driven microtome. The majority of the paraffin can then be removed by washing with a solvent and the sample swelled overnight. Following this, the sample is reduced, the excess reagent destroyed with ethanol containing NH_4NO_3 and the mixture titrated.

The usual solvents for $LiAlH_4$ are ethers. Hence, it would be convenient to be able to use ethers for the swelling medium. However, experiments with known disulfides indicated that soaking them in ethers which contain peroxides prior to reduction and titration gave low mercaptan values. These peroxides form very rapidly and avoiding them would require a more complicated experimental setup. Although we were not able to show this effect of peroxides on the mercaptan values obtained on reduced vulcanizates, it was considered best to eliminate this possible source of error. *n*-Hexane appeared to be satisfactory as a solvent for the removal of paraffin and as a swelling medium.

TABLE II

DETERMINATION OF DI-TERT-BUTYL DISULFIDE AND DI-TERT-BUTYL TRISULFIDE BY REDUCTION WITH $LiAlH_4$ FOLLOWED BY POTENTIOMETRIC TITRATION

	Millimoles added	Millimoles found		% Recovery
		Sulfide	Mercaptan	
Di-tert-butyl disulfide	0.0447_5	0.0000	0.0923	103.1
Di-tert-butyl trisulfide	0.0307_3	0.0253	0.0645	97.4

Various ethers were tested as solvents for $LiAlH_4$. The reaction was more rapid in THF than in any of the other ethers which were tested. The presence of *n*-hexane in the THF did not interfere with the reduction or with the subsequent titration.

By controlling the quantities of *n*-hexane, THF and ethanol, it is possible to prevent the solvent mixture from separating into two layers on addition of ammonia and during the titration. Furthermore, the quantities of paraffin normally present do not interfere. However, the balance is sensitive—when two layers are formed or when paraffin separates out as a film, *n*-hexane or ethanol—NH_4NO_3 is added to stabilize the solution.

Ammonium nitrate is added as a buffer. It also increases the conductivity of the background solution which is desirable for the potentiometric titration.

EXPERIMENTAL PROCEDURE

Preliminary extraction and treatment with ether-HCl.—The rubber vulcanizate in the form of a tensile slab (approximately 0.075 inch) is passed three times through a cold, closed mill. 1.5 g samples are extracted with chloroform for 7 days in a Soxhlet extractor. The samples are then vacuum dried for 24 hours at room temperature (ca. 0.05 mm with pure nitrogen bled into the drying

TABLE III

PHYSICAL DATA

Compound No.		115	116	117	118	119	120	121	122
Natural rubber		100.	100.	100.	100.	100.	100.	100.	100.
Philblack O (HAF)		—	50.	—	50.	—	50.	—	50.
Zinc oxide		5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Laurex		3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Sulfur		—	—	3.00	3.00	3.00	3.00	3.00	3.00
TMTD		3.50	3.50	—	—	—	—	—	—
MBT		—	—	1.00	1.00	—	—	—	—
808		—	—	—	—	1.00	1.00	—	—
DPG		—	—	—	—	—	—	1.00	1.00
Total		111.50	161.50	112.00	162.00	112.00	162.00	112.00	162.00
	Cure								
300% modulus (psi)	15′	175	2180	200	1825	230	1840	75	1175
	30′	180	2340	240	2325	375	2500	110	1800
	45′	190	2340	250	2325	340	2700	170	2170
	60′	200	2420	240	2440	300	2850	190	2400
	120′	200	2540	230	2440	220	2610	225	2600
Tensile strength (psi)	15′	2960	3720	3980	3890	4085	4225	1860	3150
	30′	2800	3625	3850	4000	4560	4425	2700	3920
	45′	2690	3660	3500	3800	4225	4100	3000	4080
	60′	2740	3660	2940	3700	4060	4060	3360	4080
	120′	2850	3590	3110	3500	3360	3660	3210	3675
Elongation @ break (%)	15′	750	470	810	540	785	585	850+	580
	30′	695	425	765	470	705	505	830	550
	45′	690	430	740	440	705	440	800	520
	60′	690	420	730	415	700	420	765	470
	120′	695	415	745	400	760	395	740	405
Shore A hardness	15′	37	66	39	65	42	64	27	58
	30′	38	68	41	70	45	70	34	63
	45′	39	68	41	71	46	72	37	67
	60′	38	68	41	71	45	73	40	70
	120′	38	69	40	71	41	72	41	72

apparatus). They are then refluxed for one hour in 75 ml of reagent-grade ether to swell the samples. Ten ml of concd. HCl are then added, and the samples are refluxed for an additional three hours while nitrogen is swept through the apparatus. The hydrogen sulfide is collected in acidified aqueous cadmium acetate (25 g cadmium acetate and 100 ml glacial acetic acid per l). The sulfide sulfur is then determined iodiometrically. The excess ether-HCl is decanted and the samples washed with deionized water and blotted dry. They are then extracted for 48 hours with reagent-grade methanol, returned to the drying apparatus and vacuum dried for 48 hours at room temperature with a nitrogen bleed.

Preparation for microtoming.—Five hundred mg of the chloroform extracted-ether-HCl treated samples are placed in a flat-bottom glass cylinder and covered with 10 ml paraffin heated to approximately 60° C. The samples are impregnated with the liquid paraffin by evacuating the cylinder for approximately five minutes while the temperature is maintained at 60°. The vacuum is released and the cylinder re-evacuated to check the removal of air. The rubber is pressed into the bottom of the cylinder using an aluminum plunger, on the bottom of which is a stainless steel screen which fits the cylinder very closely. The paraffin is cooled, then the cylinder is heated to remove the sample imbedded in paraffin and the plunger is removed by gentle heating. Then more liquid paraffin is poured over the rubber plug to form a paraffin foot.

Slicing on microtome.—The paraffin foot is warmed and attached to the freezing attachment of the microtome (American Optical Company Model 880). The microtome is set to slice at 5 microns, and the sample is cooled with dry ice. The blade is also cooled during the microtoming operation by a basket of dry ice which fits against the knife. The slicing is done at approximately three

strokes per second. If run too slowly, the knife knocks the paraffin plug from the cooling attachment. The slices are collected in a beaker using a metal funnel.

Extraction of paraffin and swelling.—The slices are washed over a coarse filter paper using about 50 ml *n*-hexane. They are then transferred to the reaction flask using about 20 ml *n*-hexane. (The reaction flask is a 125 ml round-bottom flask with a connection for a condenser and two sidearms for introducing dry nitrogen and for the addition of reagents and a trap containing 3 ml conc. NH_4OH at the top.) The samples are soaked overnight with the flask connected to the condenser and with the sidearms stoppered.

Reduction and titration of rubber sample.—The reaction flask is swept with a slow stream of nitrogen and cooled in an ice bath. Thirty ml treated THF (THF with enough dissolved $LiAlH_4$ in this solvent and indicator to give a faint pink color) are added through the sidearm. A rubber stopple is inserted in the larger sidearm and 3 ml $LiAlH_4$-THF solution (for preparation, see below) added dropwise using a syringe with needle. The addition is slow at first, but then more rapid. About five minutes are taken for the addition. The reaction flask is then placed in a 25° C water bath for three hours and the mixture stirred with a magnetic stirrer. The excess $LiAlH_4$ is then destroyed by adding 10 ml of 0.5% NH_4NO_3-ethanol solution. This solution is added dropwise at first until the evolution of hydrogen ceases, and then the remainder is squirted in. Next, the 3 ml conc. NH_4OH in the trap are added through the condenser and rinsed with 20 ml NH_4NO_3-ethanol solution. The contents of

TABLE IV

SULFUR GROUP ANALYSES OF CROSSLINKS

Compound No.		115	116	117	118	119	120	121	122
Cure system		TMTD "Sulfurless"		MBT+sulfur		808+sulfur		DPG+sulfur	
Type of stock		Gum	Black	Gum	Black	Gum	Black	Gum	Black
	Cure								
Millimoles S^{--}/g (after reduction)	15′	.0108	.0036	.1486[1]	.0429[2]	.1548	.0636	.0906	.0366
	30′	.0144	*.0008	.1134[2]	.0585[3]	.2208	.0846	.1494	.0930
	45′	.0054	*.0012	.0909[3]	.0567[2]	.1675[2]	.0930	.1788	.0560[4]
	60′	.0036	*.0006	.0840[3]	.0435[3]	.1314[3]	.0798	.1512	.0828
	120′	.0054	Trace	.0423[3]	.0180[3]	.0762[3]	.0348	.1212	.0552
Millimoles RSH/g (after reduction)	15′	.0252	.0072	*.1138[1]	*.0576[2]	.0540	.0504	*.0468	.0432
	30′	.0180	.0042	*.1512[2]	.0774[3]	.1044	*.0720	.0612	.0684
	45′	.0108	.0042	*.1206[3]	.0720[2]	*.0952[2]	.0792	*.1008	.0604[4]
	60′	.0108	.0030	*.1134[2]	.0630[3]	.1402[3]	.0792	*.1332	.0684
	120′	.0072	.0036	*.0774[3]	.0360[3]	.0936[3]	.0576	*.1548	.0468
"Rubber," cc/g sample (after *n*-heptane extraction)[5]	15′	1.033	.704	1.025	.712	1.024	.712	1.034	.713
	30′	1.031	.704	1.020	.708	1.023	.711	1.029	.711
	45′	1.030	.705	1.018	.707	1.021	.709	1.026	.711
	60′	1.031	.705	1.018	.706	1.020	.708	1.024	.710
	120′	1.033	.704	1.018	.707	1.020	.709	1.021	.707
$10^4 \times$total crosslinks (moles/cc rubber)	15′	.44	.78	.58	.77	.55	.70	.25	.44
	30′	.51	.84	.69	1.08	.76	1.09	.39	.72
	45′	.53	.85	.69	1.18	.80	1.26	.50	.86
	60′	.54	.85	.69	1.19	.78	1.34	.58	1.00
	120′	.54	.86	.66	1.19	.67	1.23	.66	1.14
$10^4 \times$R—S—S_x—S—R crosslinks (moles/cc rubber)[4]	15′	.12	.05	.55	.40	.26	.35	.23	.30
	30′	.09	.03	.74	.55	.51	.51	.30	.48
	45′	.05	.03	.59	.51	.47	.56	.49	.42
	60′	.05	.02	.56	.45	.70	.56	.65	.48
	120′	.03	.03	.38	.25	.46	.41	.76	.33
$10^4 \times$R—S—R crosslinks (moles/cc rubber)[4]	15′	.32	.73	.03	.37	.29	.35	.02	.14
	30′	.42	.81	[−.05]	.53	.25	.58	.09	.24
	45′	.48	.82	.10	.67	.33	.70	.01	.44
	60′	.49	.83	.13	.74	.08	.78	[−.07]	.52
	120′	.51	.83	.28	.94	.21	.82	[−.10]	.81

TABLE IV (*Continued*)

Compound No.		115	116	117	118	119	120	121	122
Cure system		TMTD "Sulfurless"		MBT + sulfur		808 + sulfur		DPG + sulfur	
Type of stock	Cure	Gum	Black	Gum	Black	Gum	Black	Gum	Black
$10^4 \times$g-a S^{--}/cc Rubber (after reduction)	15′	.10	.05	1.45	.60	1.51	.89	.88	.51
	30′	.14	.01	1.11	.83	2.16	1.19	1.45	1.31
	45′	.05	.02	.88	.80	1.64	1.31	1.74	.79
	60′	.03	.01	.83	.62	1.29	1.13	1.48	1.17
	120′	.05	Trace	.42	.25	.75	.49	1.19	.78
X in R—S—S_x—S—R[6]	15′	(.9)	(1.0)	2.6	1.5	5.7	2.5	3.9	1.7
	30′	(1.6)	(.4)	1.5	1.5	4.2	2.4	4.9	2.7
	45′	(1.0)	(.6)	1.5	1.6	3.5	2.3	3.5	1.9
	60′	(.7)	(.4)	1.5	1.4	1.9	2.0	2.3	2.4
	120′	(1.5)	(.0)	1.1	1.0	1.6	1.2	1.6	2.4
$10^4 \times$total sulfur in crosslinks (g-a/cc rubber)	15′	(.67)	(.88)	2.59	1.78	2.32	1.95	1.35	1.26
	30′	(.73)	(.88)	2.59	2.45	3.43	2.78	2.14	2.51
	45′	(.64)	(.90)	2.16	2.49	2.90	3.13	2.74	2.08
	60′	(.63)	(.88)	2.07	2.25	2.77	3.02	2.78	2.65
	120′	(.63)	(.88)	1.46	1.70	1.87	2.12	2.70	2.25
Average no. of S-atoms/crosslink	15′	(1.52)	(1.13)	4.5	2.3	4.2	2.8	5.4	2.9
	30′	(1.43)	(1.05)	3.8	2.3	4.5	2.6	5.5	3.5
	45′	(1.21)	(1.06)	3.1	2.1	3.6	2.5	5.5	2.4
	60′	(1.17)	(1.04)	3.0	1.9	3.6	2.3	4.8	2.7
	120′	(1.17)	(1.02)	2.2	1.4	2.8	1.7	4.1	2.0
% of total crosslinks of R—S—S_x—S—R type	15′	(27)	(6)	95	52	47	50	92	68
	30′	(18)	(4)	107	51	67	47	77	67
	45′	(9)	(4)	86	43	59	44	98	49
	60′	(9)	(2)	81	38	90	42	112	48
	120′	(6)	(3)	58	21	69	33	115	29
% of organically combined sulfur in crosslinks	15′	(60)	(86)	58	57	69	63	69	56
	30′	(75, 92)	(200)	41	49	72	59	68	69
	45′	(64)	(120)	35	43	54	57	68	51
	60′	(61)	(94)	33	36	50	54	60	53
	120′	(59)	(104)	24	29	39	40	47	42

* Potentiometric titration break doubtful.
[1] Average of three values.
[2] Average of two values.
[3] Determined from specific volume of the vacuum-dried sample after contact with *n*-hexane for 6 days during the swelling test for crosslinks. Correction for volume of zinc oxide and carbon black in the sample was based on specific gravities of 5.56 and 1.80 respectively. Correction was also made for material extracted during the test.
[4] One-half the mercaptan values when expressed in moles/cc rubber phase.
[5] (Total crosslinks)—(R—S—S_x—S—R crosslinks).
[6] $\frac{\text{Sulfide sulfur after reduction}}{0.5 \times \text{Mercaptan sulfur after reduction}}$.

the reaction flask are then transferred to a 250-ml beaker using 70 ml NH_4NO_3-ethanol solution.

Titration.—The solution containing the treated rubber is titrated with aqueous 0.1 *N* $AgNO_3$ using increments of 0.018 ml (Micro-Metric Instrument Company, Cleveland, Ohio, Syringe Microburet Model No. SB-2). A silver-calomel electrode system is used. As the endpoint is approached, the additions are made at one-minute intervals. The MV^- potential readings are taken with a potentiometer. The sulfide break is usually found between 600 and 450 MV^-, and the mercaptan break between 330 and 150 MV^-. Sulfide and mercaptan values are obtained from these breaks. The sulfide break is titrated rapidly, but the mercaptan break requires more time to reach equilibrium between additions. At the endpoint, the additions are made at one-minute intervals on both sulfide and mercaptan breaks.

$$S^{--} \quad \frac{\text{ml} \times \text{normality } (AgNO_3)}{2} = \text{millimoles, sulfide sulfur}$$

$$RSH \quad \text{ml} \times \text{normality } (AgNO_3) = \text{millimoles, mercaptan sulfur}$$

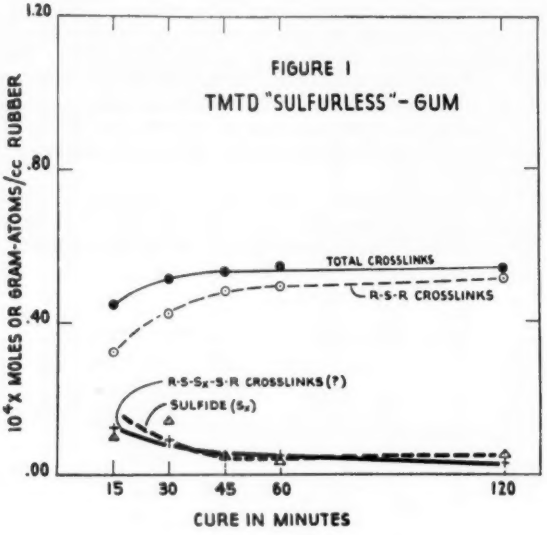
Preparation of reagents.—(1) $LiAlH_4$-THF solution. THF is distilled from $LiAlH_4$ ($LiAlH_4$ is added until there is no evidence of further reaction). Then about 18 g $LiAlH_4$ are added to 180 ml of the distilled THF. The mixture is stirred and allowed to stand overnight. It is then filtered through glass wool and three drops of indicator added (1% 4-phenylazo-diphenylamine in benzene). The indicator shows the presence of $LiAlH_4$, but is not active in the *absolute* absence of water as when the reagent solution is allowed to stand for a prolonged period of time.

(2) NH_4NO_3-ethanol solution. Ethanol was obtained by distilling specially denatured alcohol (formula 23A) and selecting the 73° C fraction (at 620 mm Hg). Five g NH_4NO_3 are dissolved in 1 l of distilled ethanol.

TABLE V

VARIOUS ANALYSES ON WEIGHT PER CENT BASIS

Compound No.		115	116	117	118	119	120	121	122
Cure system		TMTD "sulfurless"		MBT + sulfur		808 + sulfur		DPG + sulfur	
Type of stock	Cure	Gum	Black	Gum	Black	Gum	Black	Gum	Black
Wt. % S^{--} sulfur (after reduction)	15′	0.03	0.01	0.37 .55, .51	0.13 .15	0.50	0.20	0.29	0.12
	30′	.05	.00₃	.35 .38	.17 .20	.71	.27	.48	.30
	45′	.02	.00₄	.28 .31	.17 .20	.50 .57	.30	.57	.24 .10, .20
	60′	.01	.00₂	.24 .30	.17 .11	.45 .39	.26	.49	.27
	120′	.02	Trace	.13 .14	.05 .06	.23 .26	.11	.39	.18
Wt. % RSH sulfur (after reduction)	15′	.08	.02	.38 .41, .30	.19 .19	.17	.16	.15	.14
	30′	.06	.01	.51 .46	.24 .25	.34	.23	.20	.22
	45′	.03	.01	.37 .40	.22 .24	.24 .37	.25	.32	.16 .16, .25
	60′	.03	.01	.31 .42	.19 .22	.46 .43	.25	.43	.22
	120′	.02	.01	.27 .23	.10 .13	.25 .35	.19	.50	.15
Wt. % total sulfur (after extraction and ether-HCl treatment)	15′	.37	.42	1.48	.90	1.10	.90	.65	.71
	30′	.32 .26	.29	2.06	1.33	1.56	1.26	1.04	1.02
	45′	.33	.36	2.02	1.51	1.75	1.43	1.33	1.12
	60′	.34	.40	2.07	1.61	1.82	1.46	1.52	1.33
	120′	.35	.38	1.97	1.50	1.58	1.39	1.88	1.41
Wt. % free sulfur (untreated samples)	15′	—	—	.82	.84	.90	.86	1.76	1.20
	30′	—	—	.18	.35	.31	.40	1.35	.86
	45′	—	—	.04	.13	.11	.17	.98	.58
	60′	—	—	.02	.04	.05	.06	.67	.36
	120′	—	—	.02	.02	.03	.02	.18	.07
Wt. % inorganic sulfide (untreated samples)	15′	.01	.02	.25	.13	.38	.16	.10	.08
	30′	.03	.04	.40	.25	.59	.30	.21	.18
	45′	.05	.05	.47	.32	.72	.40	.31	.27
	60′	.06	.05	.51	.38	.78	.47	.42	.36
	120′	.09	.08	.59	.43	.89	.60	.70	.58



RESULTS

The compounds studied and stress-strain and Shore hardness data are tabulated in Table III. No sample was allowed to age more than two weeks at room temperature between the time it was vulcanized and the time it was extracted. The analytical data and certain values calculated from them are presented in

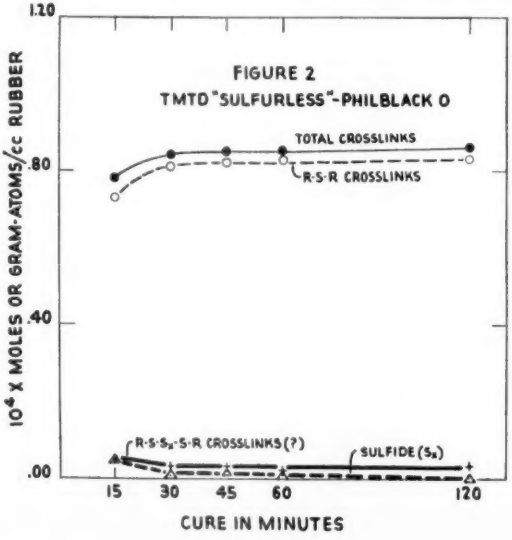
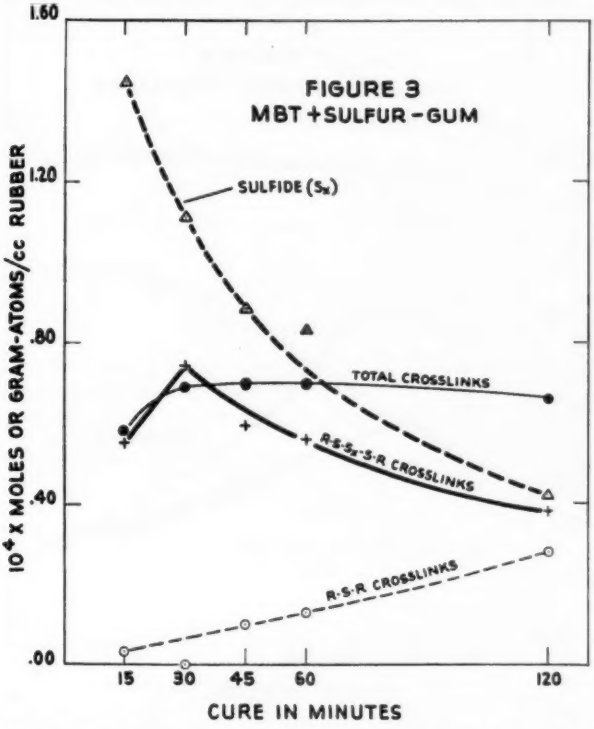


Table IV. After each of the forty samples (five cures for each of eight compounds) were analyzed, the data were plotted against time of cure. Reasonably smooth curves were obtained for most of the compounds. The most serious irregularity in the data was observed in the mercaptan values for the 808-sulfur-gum stock and in both sulfide and mercaptan values for the DPG-sulfur-Philblack O stock. Analyses of certain cures thought to be out of line were repeated. Where more than one analysis was made on a given sample, the average value is listed in Table IV and plotted in the figures. (Table V contains all analytical values.)

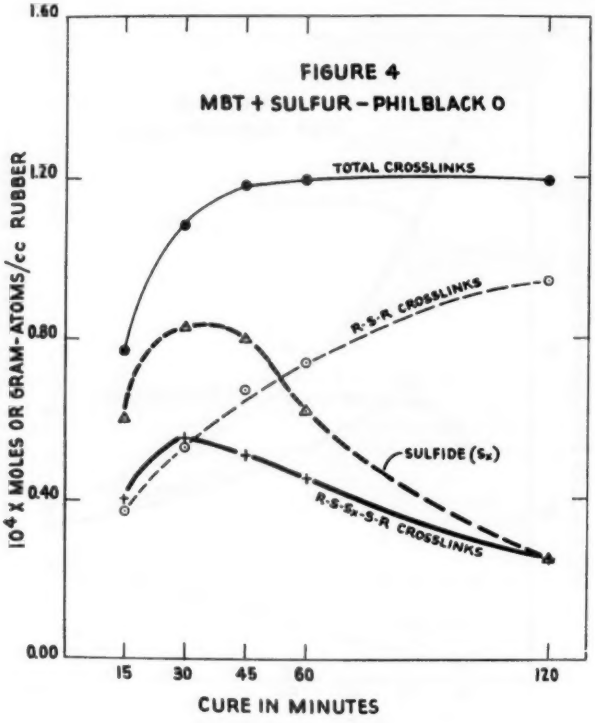


To check the reproducibility of the analyses, all cures of the MBT-sulfur-gum and Philblack O stocks were run in duplicate. These and all other analytical values are presented in Table V, where the values are expressed as weight per cent sulfur in mercaptan and in sulfide form after reduction with $LiAlH_4$. In spite of the poor mercaptan breaks observed with all cures of the gum stock and the 15-min cure on the Philblack O stock, the reproducibility seems reasonably good.

Each R—S—S_x—S—R crosslink, where $x = 0$ for disulfide and x is finite for polysulfides, should give two molecules of mercaptan on reduction. If we express the total crosslinks and the R—S—S_x—S—R crosslinks ($\frac{1}{2}$ the RSH by analysis) in the same units, we can obtain the R—S—R crosslinks by difference.

Here, it is assumed that only R—S—R, R—S—S—R and R—S—S_x—S—R crosslinks are present in the vulcanizates studied.

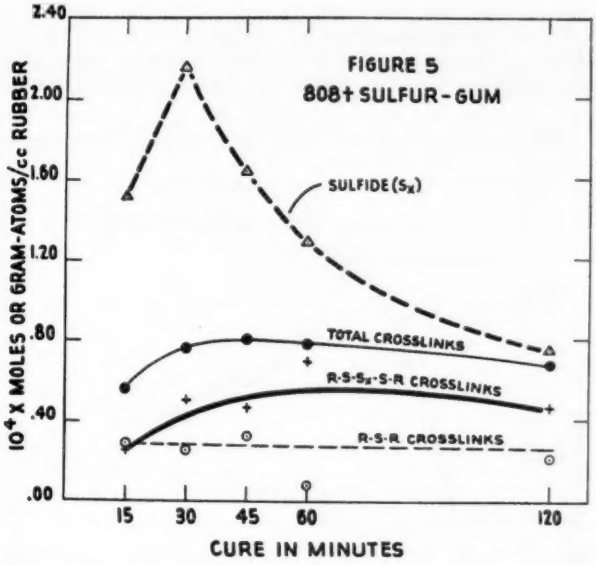
The results, so obtained, are plotted against time of cure in Figures 1 through 8. All values are expressed in moles/cc "rubber". In this calculation, the specific volumes obtained on the swollen and dried samples during the swelling tests are corrected for the volume of zinc oxide and carbon black, if present. The zinc oxide and carbon black were considered as inert pigments, e.g. no volume change during vulcanization. The total crosslinks were corrected for



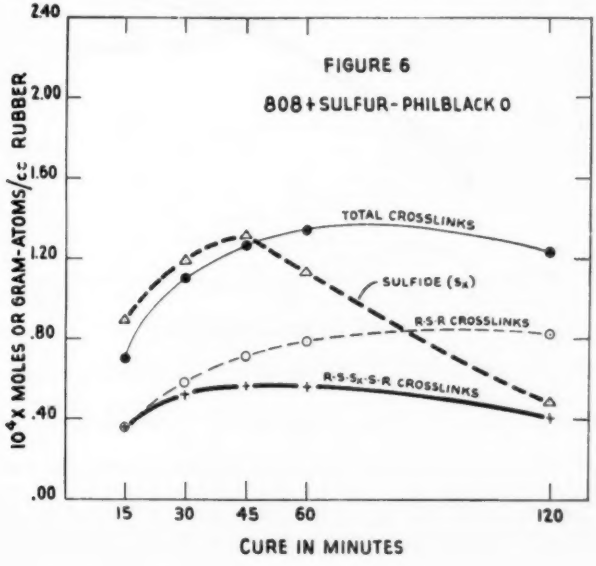
the material extracted during the swelling tests. This correction was also applied to the mercaptan and sulfide values, although, strictly speaking, the correction in this case should have been based on the quantity of material removed by the chloroform extraction, the treatment with ether-HCl and methanol extraction.

DISCUSSION

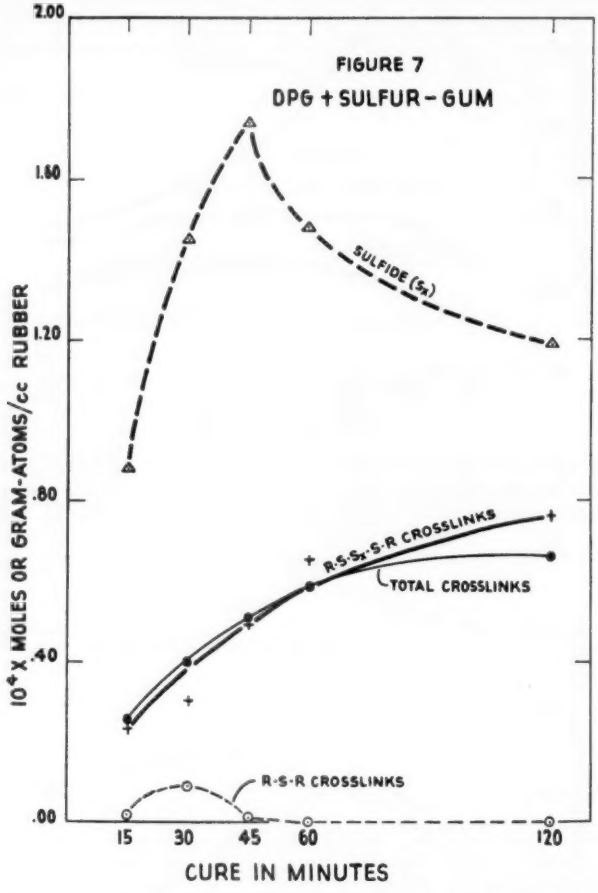
Figures 1 and 2 indicate that monosulfides are the predominant type of crosslink in the TMTD "sulfurless" cures. Of course, carbon-to-carbon bonds would be included with our monosulfide values. However, Moore's experiments on TMTD "sulfurless" gum stocks indicate that the crosslinks contain sulfur[3].



We do not know that the small mercaptan and sulfide values on these TMTD "sulfurless" cures represent sulfur derived from R—S—S_x—S—R crosslinks. The reagent, $LiAlH_4$, slowly attacks diallyl monosulfide (Table VI); and it was

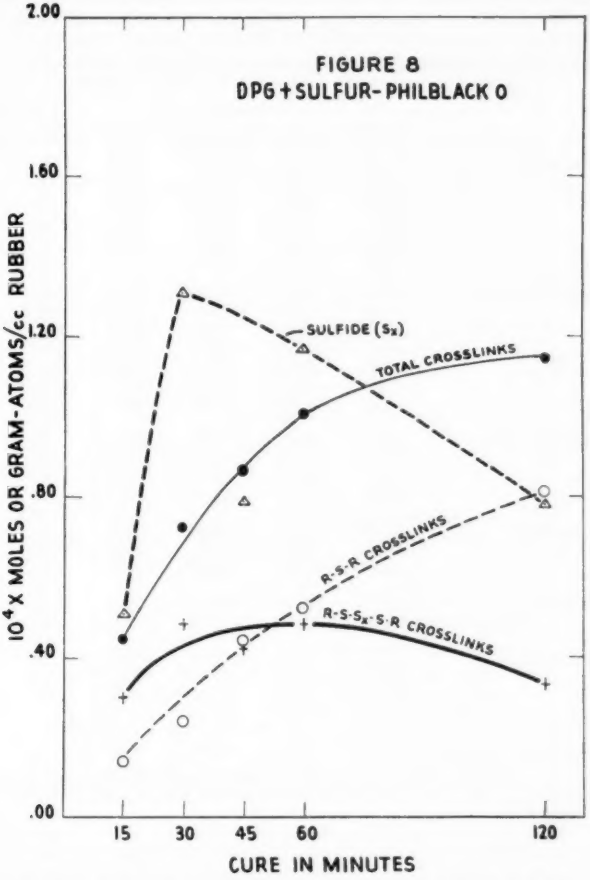


thought that it might also attack diallyl or allyl-alkyl monosulfidic crosslinks, which we feel are the dominant type of crosslink in these TMTD "sulfurless" cures. However, time studies to be reported elsewhere make this type of attack seem doubtful as the sole source of the small mercaptan and sulfide values found.



$LiAlH_4$ is a very powerful, although somewhat selective, reducing agent. It will attack the C—S linkage in compounds containing the —N—C—S— grouping[15]. This provides another possible source of the traces of mercaptan and sulfide sulfur which were found in the TMTD "sulfurless" cures. Bevilacqua[16] has suggested that dithiocarbamoyl esters are formed by addition of dithiocarbamoyl radicals to rubber molecules during TMTD "sulfurless" cures.

He felt that these dithiocarbamoyl esters were hydrolyzed with catalysis by zinc ions leading finally to disulfide crosslinks. If they are present in our samples, they could well be the source of the mercaptan and sulfide ions which we found by analysis. In this case, the quantities of monosulfide crosslinks and the total crosslinks would be identical, since the crosslinks in TMTD cures have been shown to contain sulfur[3].



The only other indication of a single type of bond is in the *DPG-accelerated gum stock*, Figure 7. *Here, the correspondence between the R—S—S_x—S—R type bonds, as measured by* $\frac{RSH}{2}$, *and the total crosslinks may be within the experimental error over the entire curing range.* These results may be compared with those of Flory, Rabjohn and Shaffer[17] where the "quantitative" crosslinking agent, decamethylene dismethylazodicarboxylate, was used. (See also, how-

ever, Moore and Watson[18].) *In all the other rubber compounds studied, the total crosslinks are greater than the R—S—S_x—S—R type; and, on the basis of our assumptions, this would indicate the presence of some monosulfidic crosslinks.*

The recent studies of Bateman et al.[1] on model systems and of Dogadkin[9] on accelerated sulfur vulcanizates indicate that polysulfide crosslinks are formed during the early stages of cure. Subsequently, these are partially converted into groups which contain less sulfur per crosslink and also into cyclic sulfides

TABLE VI

TYPICAL DETERMINATIONS ON KNOWN SULFUR COMPOUNDS RUN BY PROCEDURE USED FOR RUBBER SAMPLES

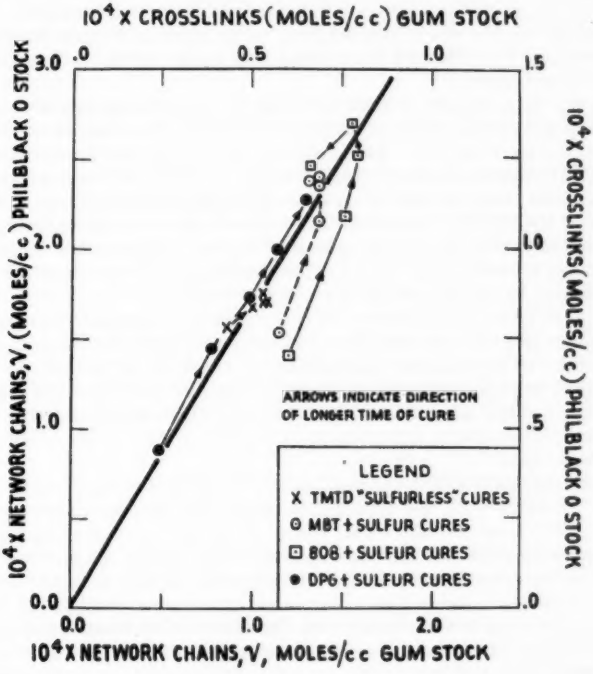
	Millimoles added	Millimoles found			% of theoretical	
		Sulfide	Mercaptan	Total	Sulfide	Mercaptan
Diphenyl disulfide	.0189	.0000	.0348	.0348	—	92.1
	.0195	.0000	.0360	.0360	—	92.3
	.0244	.0000	.0486	.0486	—	99.6
	.0161	Trace	.0306	.0306	—	95.0
	.0207	Trace	.0415	.0415	—	100.2
	.0366	.0020	.0690	.0710	—	94.3
Di-tert-butyl trisulfide	.0409	.0435	.0666	.1101	106.4	81.4
	.0185	.0192	.0324	.0516	103.8	87.6
	.0273	.0294	.0480	.0774	107.7	87.9
	.0216	.0252	.0372	.0624	116.7	86.1
	.0250	.0278	.0391	.0669	111.2	78.2
	.0282	.0310	.0467	.0777	109.9	82.8
	.0245	.0258	.0436	.0694	105.3	89.0
Di-tert-butyl disulfide	.0257	.0072	.0486	.0558	—	94.6
	.0613*	.0612*	.0522*	.1134*	—	42.6*
	.0323	.0098	.0465	.0563	—	72.0
	.0303	.0130	.0424	.0554	—	70.0
Dibenzyl disulfide	.0183	.0072	.0288	.0360	—	78.7
	.0196	.0223	.0135	.0358	—	34.4
	.0411	.0140	.0650	.0790	—	79.1
Diallyl disulfide	.0317	.0204	.0337	.0541	—	53.1
	.0326	.0314	.0246	.0560	—	37.7
Diallyl monosulfide	.0867	.0081	.0126	.0207	—	—
	.0471*	.0315*	.0090*	.0405*	—	—
	.0412**	.0510**	.0036**	.0546**	—	—
	.0323**	.0279**	.0036**	.0315**	—	—
Menthl-*n*-octyl monosulfide	.0484	.0000	.0000	.0000	—	—

* Reduced overnight in $LiAlH_4$ solution—all others reduced 3 hours, except as noted by **.
** Reduced over weekend. Since the first analysis gave more sulfur than was added as diallyl monosulfide, it was repeated.

which do not contribute to crosslinking. The data plotted in Figures 3 through 8 are in complete accord with this picture. It is of interest that in the initial phase of vulcanization, the polysulfide sulfur, S_x, reaches much higher values in gum stocks than in the corresponding Philblack O stocks. During this early stage of cure, the carbon black restricts the formation of long polysulfide chains. It may do this by decreasing their stability or perhaps by directing the reactions to an alternate course and hence decreasing the quantity of sulfur available for polysulfide groups. In the later stages of cure, this particular difference between gum stocks and Philblack O stocks vanishes.

In each of the four types of cures, carbon black apparently promotes the formation of monosulfidic crosslinks. In fact, this appears to be the most important chemical difference between the carbon black-loaded vulcanizates and the corresponding gum stocks. With sulfur cures, this action of carbon black is believed to be due to two factors: (a) Carbon black is an effective catalyst for dehydrogenation by sulfur[19]. This would promote the activity at the α-methylene carbon atoms of rubber and enhance the quantities of sulfur groups or radicals present as intermediates at these points; but it is believed that the action of carbon black on TMTD "sulfurless" cures arises from a different type of activity. This will be treated separately elsewhere. (b) We further feel

FIGURE 9


10⁴ X CROSSLINKS (MOLES/c c) GUM STOCK
10⁴ X NETWORK CHAINS, V, (MOLES/c c) PHILBLACK O STOCK
10⁴ X CROSSLINKS (MOLES/c c) PHILBLACK O STOCK
10⁴ X NETWORK CHAINS, V, MOLES/c c GUM STOCK
0.0
0.5
1.0
1.5
2.0
3.0
ARROWS INDICATE DIRECTION OF LONGER TIME OF CURE
LEGEND
X TMTD "SULFURLESS" CURES
⊙ MBT + SULFUR CURES
⊡ 808 + SULFUR CURES
● DPG + SULFUR CURES

that diallyl di- or polysulfide crosslinks which connect α-methylene carbon atoms of rubber would be converted to monosulfide crosslinks under the action of heat and zinc compounds, if they are present in the stock. (In the absence of zinc compounds, the accelerators would probably perform this function.) It may be that this will also take place in crosslinks which are attached to only one rubber molecule at the α-methylene carbon atom, in which case, allyl-alkyl monosulfides would be produced.

Diallyl tetrasulfide decomposes readily when heated; the disulfide is more stable[20]. Zinc dust attacks diallyl disulfide at 120–30° C, forming zinc sulfide and diallyl monosulfide[21]. Zinc acetate reacts with allyl mercaptan at room

temperature to form the mercaptide, $(C_3H_5S)_2Zn$, which decomposes on heating to 100°, forming zinc sulfide and diallyl monosulfide[21]. From these considerations, we would expect a considerable amount of monosulfidic crosslinks to be formed by the carbon black-promoted action of sulfur on the α-methylene carbon atoms of rubber. These may well be mainly diallyl monosulfides, although allyl-alkyl monosulfides may also be present.

Another important difference between gum and carbon black vulcanizates is that the latter have higher crosslink densities, as measured by the swelling technique. The ratio of crosslinks for a given gum stock at a given cure to the crosslinks in the corresponding carbon black stock at the same cure approaches 0.6 as the cure progresses, Figure 9. That is, at later stages of cure, there are approximately 60% as many crosslinks in a given volume of the *rubber phase* in gum stocks as in the corresponding carbon black-loaded stocks. This, of course, applies to the stocks studied here. The actual difference between such vulcanizates is dependent on the loading and nature of the carbon black and possibly other factors[14].

With the data at hand, we can calculate the relative amount of sulfur compounded in the stocks which eventually is found in the crosslinks. The data are presented in Table IV. These values are not precise because the sulfur content of the material extracted by chloroform, ether-HCl and methanol was not determined; but the error from this source should not be large. With the exception of the TMTD "sulfurless" cures, the results for a given curing system are surprisingly similar for the gum and carbon black-loaded vulcanizates. Furthermore, viewed in this way, the *accelerated vulcanization by sulfur is more efficient* than it has been considered to be heretofore.

The quantities of sulfur present in the crosslinks of normal vulcanizates are small enough to place exacting demands upon the analytical technique. Inhomogeneities in the samples—particularly in the TMTD "sulfurless" cures—are sufficient to make the total sulfur values on micro-samples (10 mg) somewhat erratic. They are less likely to be of importance in the analyses for mercaptan and sulfide sulfur following the reduction with $LiAlH_4$ where 500-mg samples were used.

The extractions to which the samples were subjected removed some rubbery material. Furthermore, the treatments before the various analyses were not identical. The total crosslinks were run on unextracted samples; and, although corrections were made for the material extracted during the six-day swelling period in *n*-heptane, these amounts were generally smaller than the quantities removed during the seven-day chloroform extraction. Additional material was removed during the treatment with the ether-HCl mixture prior to the reductions and the organically combined sulfur determinations. The inorganic sulfide sulfurs and the free sulfur values were obtained on unextracted vulcanizates. These factors make a precise sulfur balance impossible. To obtain one, it would be necessary to determine the sulfur contents of the material removed during the various extractions; and these are frequently inhomogeneous. These complications, although real, are possibly of lesser importance in the values listed in the tables than the other experimental errors.

Generally speaking, the sulfide breaks during the potentiometric titrations are good. With some samples, the mercaptan breaks are definite; with others, very poor breaks were found; and occasionally no definite mercaptan breaks could be located. In many of these cases, if a fresh sample were taken and the analysis run exactly as before, a definite mercaptan break could be located.

Occasionally, two mercaptan breaks seemed to be present. In such cases, the first break was usually ignored, e.g. the values would be for *total mercaptan*.

In all cases, we would expect the sulfide values to be slightly high and the mercaptan values to be slightly low because the sulfide precipitates first and some mercaptan would be expected to react with the silver ions before the precipitation of the sulfide is complete. See, however, Reference 22 where it is reported that high mercaptan values are obtained when the ratio of the titer for sulfide to that for mercaptan exceeds 5. It is quite possible that this effect is of minor importance in these analyses.

Throughout these analyses, we have been forced to compromise on the time and temperature for the $LiAlH_4$ treatments. Early in our work, we felt that it would be desirable to conduct the reduction at high temperatures where degradation of the sample would take place. This might permit the titrations to be conducted with the rubber in solution rather than as a finely divided solid. This proved impractical. As the temperature of the reduction was increased, the carbon-sulfur bonds were more vigorously attacked. Low temperatures, in the 10–15° C range, slowed the reaction so as to make the analytical procedure impractical. Hence, the compromise was adopted of conducting the reduction at 25° C.

It has not been possible to establish with certainty the absolute accuracy of the present method of analysis when applied to vulcanizates. Since most of the sulfide sulfur appears to be in solution, these values probably represent the right order of magnitude. The mercaptan values are less certain. Two factors lend a measure of confidence to the results: (a) The correspondence of the *total crosslinks* from swelling measurements with the *R—S—S_x—S—R type crosslinks* (measured as mercaptan after reduction) for the DPG-sulfur-gum stocks of Figure 7. This correlation, incidentally, is quite similar to that reported by Flory[17] for his decamethylene dismethylazodicarboxylate cures. (b) Early experiments indicate that the mercaptan values for an MBT-accelerated vulcanizate did not change appreciably even after 16 days contact with excess $LiAlH_4$.

However, until more experience with the method is obtained, it may be best to consider that the method is reliable for relative comparisons of similar vulcanizates and to be cautious in exact comparisons of widely different rubber compounds.

One factor which we have not taken into account so far is *reversion*. There are a number of indications of reversion in the tables and figures. For instance, in Figure 3, the number of R—S—S_x—S—R type crosslinks at 15 min cure are virtually equal to the total crosslinks. But at 30 min cure, they exceed the total number of crosslinks calculated from swelling data. In this particular case, the effect might be attributed to experimental error. But more detailed studies on MBT + sulfur cures, now under way, indicate that the effect is real. After attaining a peak at 30 minutes, the ratio of R—S—S_x—S—R crosslinks to total crosslinks decreases continuously. This is attributed to conversion of polysulfides into monosulfides (and cyclic sulfur). Reversion is also indicated in many of the curves as a decrease in total crosslinks with the longest cures. *To the extent that reversion takes place during cure[23], the monosulfide values will be low.*

The stability of sulfides and mercaptans is quite dependent upon the nature of the groups attached to the sulfur[24], e.g. allyl, *n*-alkyl, tert-alkyl, aromatic, etc. Stability of the C—S bond to $LiAlH_4$ appears to parallel its stability to

other reagents and to heat. In Table VI, data are reported for typical determinations on known sulfur compounds which were carried out under the same procedure used in studying the rubber compounds. The rupture of the C—S bond in unstable mercaptans depends on time and temperature. Within limits, more accurate analyses can be made on the less stable disulfides by shortening the time of the reduction.

Of the monosulfides, methyl-*n*-octyl sulfide was resistant to reduction; but diallyl monosulfide was attacked. In three hours, less than one-fourth of the monosulfide was decomposed; but over three-fourths of the sample was decomposed in ca. 16 hours. Next, consider the experiments starting with disulfides. The resistance of the C—S bond to reduction, as indicated by the quantity of sulfide sulfur formed, is in the order phenyl (most stable), tert-butyl, benzyl, allyl (least stable). The stability conferred on di- and polysulfides by tertiary alkyl groups is well known[24].

The applicability of the $LiAlH_4$ reduction to the determination of polysulfides in vulcanizates and the stability of the mercaptans formed indicate that the C—S bonds of the polysulfides possess a stability comparable to that conferred by tert-alkyl groups.

Throughout this paper we have assumed that the swelling measurements can be converted directly into crosslink concentration. Strictly speaking, what the swelling tests indicate is the number of elastically effective network chains. We converted these to crosslink concentration by dividing the number of network chains by two. For our purposes here, this approximation may be adequate. In all this, we ignore dangling ends, short-circuited or double crosslinks, network entanglements, etc. Since some uncertainty still persists in interpretation of the swelling data, one might well use such terms as "effective network chains" and "apparent crosslinks"[14].

ACKNOWLEDGMENT

The fine experimental work of the Huffman Microanalytical Laboratories, Wheatridge, Colorado is gratefully acknowledged.

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VULCANIZATION OF ELASTOMERS. 22. THERMAL VULCANIZATION OF SYNTHETIC RUBBERS. I *

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INTRODUCTION

In the thiuram vulcanization of natural rubber[1], the crosslinking as measured by the change in the reciprocal equilibrium swelling, is—as we have shown[2]—a first order reaction, and proceeds at the same rate as the formation of zinc dithiocarbamate which likewise obeys a first order time law. Although the chemical kinetics of the thiuram vulcanization of synthetic rubbers such as Perbunan (NBR) and Buna (SBR) show fundamentally the same picture as in the case of natural rubber[3], yet the relationship between the crosslinking and the dithiocarbamate formation will be complicated because of the fact that synthetic rubbers undergo a spontaneous crosslinking at higher temperatures; that is, a thermal vulcanization takes place[4]. Actually, the crosslinking in the case of pure thiuram vulcanization of Perbunan is a second order process, whereas the dithiocarbamate formation follows a first order course.

Naturally, a number of questions are connected with the phenomenon of thermal vulcanization, and they must be answered if we would get a clear picture of the vulcanization of synthetic rubber. Thus we can ask if the thermal vulcanization will proceed entirely independently of a simultaneous vulcanization which is induced by vulcanizing reagents and accelerators, or will the two vulcanizations modify each other? We therefore investigated—first using Perbunan N 2818 as an example—thermal vulcanization, both with and without the addition of such compounds as are used in vulcanizations with sulfur accelerated by benzothiazolyl disulfide.

This report discusses only the thermal vulcanization of Perbunan in the presence of and in the absence of added compounds. We will go into a more detailed discussion of the results only after we have published the experiences which we have had with sulfur vulcanizations accelerated with benzothiazolyl disulfide (MBTS). Details of the experimental procedures and particularly of the quantitative analysis of the extracts obtained in some of the operations will be given also in a related publication.

EXPERIMENTAL RESULTS

SIMPLE THERMAL VULCANIZATION OF PERBUNAN N 2818

What happens with respect to swelling properties (in benzene) when Perbunan N 2818 is heated to elevated temperatures (120–150° C) is shown in Figure 1 (Ordinate: reciprocal equilibrium swelling $1/Q_t$; Abscissa: reaction time t in minutes). The Perbunan was first exhaustively extracted with methanol in a Soxhlet apparatus to free it of stabilizer and other impurities. The increase in

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe from *Kautschuk und Gummi*, Vol. 11, pages WT 325 to 331, December 1958. Tables of data have been omitted to save space.

crosslinking is shown by the slightly bowed curves, which cut the ordinate at a finite value of $1/Q_t$, thus indicating a small amount of crosslinking in the starting material. Compared with other vulcanization reactions, this process is very slow, and when the values for $1/Q_t$ are plotted against the reciprocal of the vulcanization time, it is evident that even the highest values do not come close to a limiting value. Nevertheless, other investigations, not detailed here, have shown that a limiting value of the reciprocal equilibrium swelling (cross-

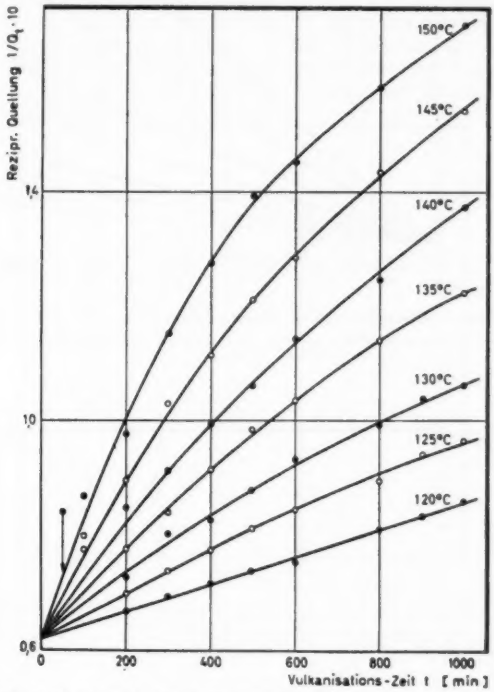

FIG. 1.—Dependence of reciprocal equilibrium swelling on the reaction time at various temperatures (pure thermal vulcanization of Perbunan). Ordinate: Reciprocal swelling, $1/Q_t \times 10$. Abscissa: Vulcanization time, t (min).

linking) is reached, which is—and this is noteworthy—independent of the temperature. In the case mentioned, $1/Q_\infty = 0.25$. This is a value notably higher than the highest value of $1/Q_t$ in Figure 1.

Figure 2 shows that the process of crosslinking can be expressed as a second order reaction, because straight lines are obtained by plotting $1/(1/Q_\infty - 1/Q_t)$ against the time of reaction. Although the whole reaction range was not included in the measurements, the points lie so closely on the straight lines, that a second order reaction may be considered to be established and hence the rate constants k_{QII} may be calculated. When these values are plotted on a logarithmic scale against the reciprocal of the absolute temperature, the straight line I of Figure 3 is obtained. From the slope of this line, the activation energy is calculated to be 23.3 kcal/mole.

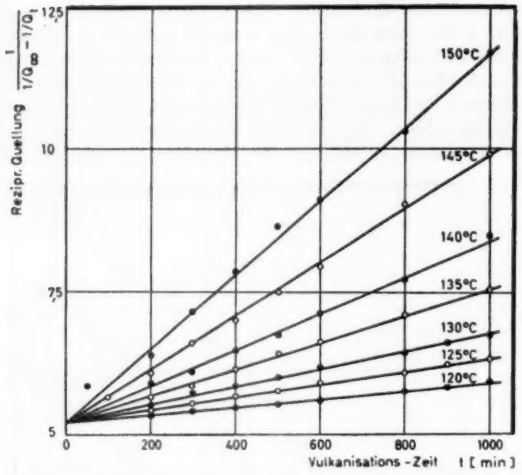

FIG. 2.—Pure thermal vulcanization of Perbunan as a second order process at various temperatures. Ordinate: Reciprocal swelling, $\frac{1}{(1/Q_\infty - 1/Q_t)}$. Abscissa: Vulcanization time, t (min).

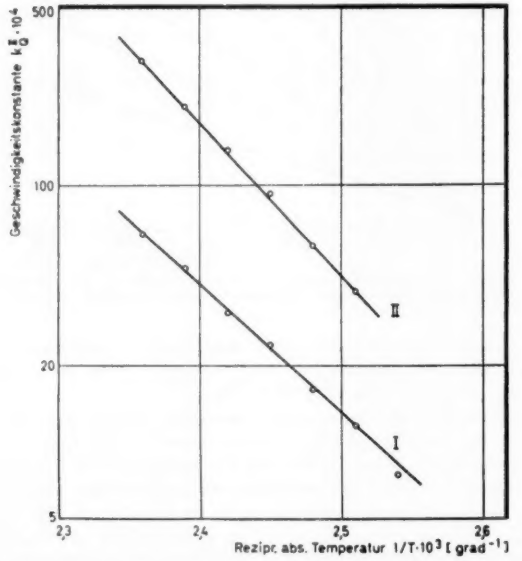

FIG. 3.—Dependence on temperature of the rate constant of the second order process of pure thermal vulcanization (I) as well as of the thermal vulcanization of Perbunan accelerated with MBTS (II). Ordinate: Rate constant, $k_Q^{II} \times 10^4$. Abscissa: Reciprocal abs. temp., $1/T \times 10^3$ degree^{-1}.

Of the ethylene monomers, styrene and methyl methacrylate show definite thermal polymerization. In solution and at high dilution, the thermal polymerization of styrene is a second order reaction; when concentrated solutions are used a reaction order between first and second is noted, and a thermal block polymerization[6] was found to follow a first order course. The activation energy of the thermal polymerization of styrene is given as 23 kcal/mole[7].

Since natural rubber, as *cis*-1,4-polyisoprene, shows no thermal crosslinking, we may well conclude that thermal vulcanization of Perbunan takes place because of the vinyl side chains on the threadlike molecules which side chains result from a 1,2-addition polymerization. The $-CH=CH_2$ groups may be considered as monomers fixed on the chain molecules and thus limited in their mobility, while the whole molecular network acts as solvent material. Looked

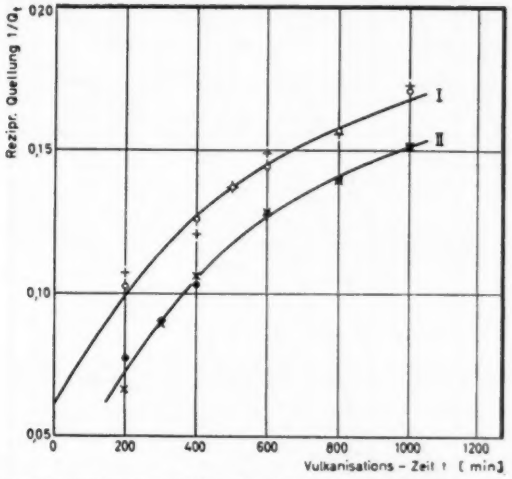

FIG. 4.—Inhibition by hydroquinone of thermal vulcanization of Perbunan. Curve I: pure thermal vulcanization; (o and +) are thermal vulcanizations in the presence of varying amounts of benzoquinone. Curve II: thermal vulcanization in the presence of various amounts of hydroquinone (● or x). Ordinate: Reciprocal swelling, $1/Q_t$. Abscissa: Vulcanization time, t (min).

at in this way, there is a certain analogy between thermal polymerization in solution and thermal vulcanization, and this conception suggests similar orders of reaction much more than it does the same activation energies.

Bimolecular formation of biradicals seems to be the most logical chain-initiating reaction in thermal polymerization, for in this way the kinetics of the whole reaction can best be clarified. Thorough study indicates, however, that the building of very long chain molecules does not fit this conception very well, but that the formation of cyclic products of low molecular size is much more likely[8]. When we consider furthermore that thermal polymerization rarely takes place—many cases of this kind have been shown by careful investigation to be induced polymerizations—we will have reservations in regard to explanations of thermal vulcanization. The simultaneous occurrence of vinyl and allyl groups in synthetic rubbers especially complicates the picture, and in addition adequate purity of the starting materials for evaluation of the relations cannot be guaranteed (peroxide content, for example?!)

THERMAL VULCANIZATION OF PERBUNAN N 2818 CONTAINING ADDITIVES, PARTICULARLY MBT AND MBTS

Thermal vulcanization in the presence of hydroquinone and mercaptobenzothiazole (MBT).—There need be no doubt that the thermal vulcanization of Perbunan involves a radical mechanism, and yet the addition of benzoquinone shows neither a slowing nor acceleration of the process. On the other hand, hydroquinone exerts a pronounced inhibition. This is shown in a comparison of Curves I (simple thermal vulcanization) and II (addition of hydroquinone) in Figure 4. After the induction period, the thermal vulcanization (II) goes

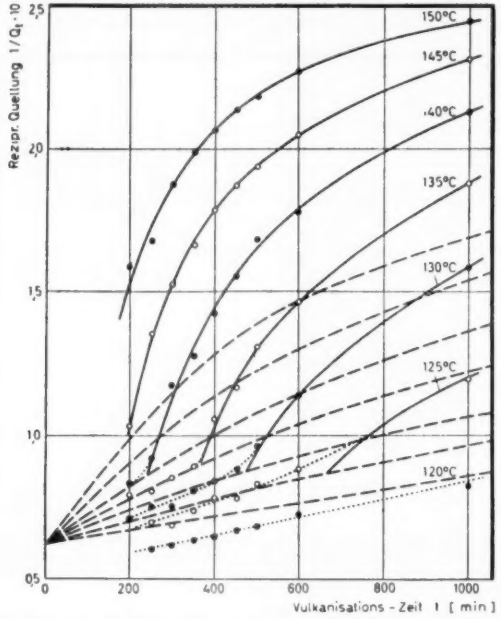

FIG. 5.—Dependence of reciprocal equilibrium swelling of Perbunan on time of reaction at various temperatures. Broken lines are for pure thermal vulcanizations; solid lines are for thermal vulcanizations accelerated with a constant initial amount of MBTS. Ordinate: Reciprocal swelling, $1/Q_t \times 10$. Abscissa: Vulcanization time, t (min).

at the same rate as in the absence of hydroquinone (I), indicating a true inhibitory behavior[9]. Yet, the independence of the induction period on concentration of hydroquinone is noteworthy; right now we see no explanation for this.

Quite different behavior is noted when increasing amounts of MBT are added to Perbunan. We dispense with the description of the experiments, which were carried out at 150° C, due to lack of space and confine ourselves to the presentation of essential results.

MBT produces an important increase in the rate of thermal vulcanization and the rate rises with an increase in MBT content. This activating effect of MBT is not immediately noticeable, but an induction period is noted for the acceleration which period decreases as the MBT content is increased. The

thermal vulcanization proceeds without modification during the induction period before the acceleration begins. The acceleration sets in suddenly in every case.

The action of the MBT is confined to the acceleration or activation, that is, there is no simultaneous increase in crosslinking. This is shown by ascertaining the limiting value of the equilibrium swelling which is found to be $1/Q_\infty = 0.25$. This is the same as for pure thermal vulcanization. It can be seen how easily the idea can be arrived at, when no attention is paid to the limiting value of the equilibrium swelling, that MBT serves as a vulcanizing agent for Perbunan. The crosslinking in the presence of MBT is a second order process, and the rate constant is an increasing function of the initial MBT concentration (MBT).

Thermal vulcanization in the presence of benzothiazolyl disulfide (MBTS).—MBTS has an effect similar to that of MBT. Careful studies were conducted on this. At first we studied the effect of temperature on the thermal vulcanization in the presence of a constant amount of MBTS (3.325 g in 100 g rubber

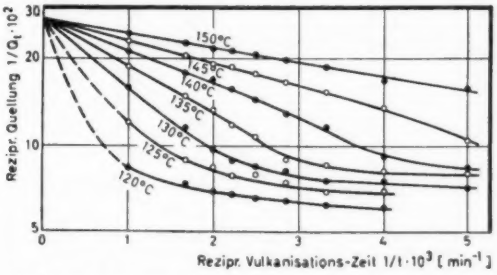

FIG. 6.—Determination of the limiting equilibrium swelling for the thermal vulcanization of Perbunan accelerated with MBTS. Ordinate: Reciprocal swelling, $1/Q_t \times 10^2$. Abscissa: Reciprocal vulcanization time, $1/t \times 10^3$ (min^{-1}).

compound). The data on swelling measurements obtained in this work are given graphically in Figure 5. The broken lines are those of Figure 1 for the pure thermal vulcanization, while the solid lines to which also the dotted lines are joined, show the course of the vulcanization in the presence of MBTS.

It can be seen that MBTS also is a very effective accelerator—at least at temperatures above 120° C—and fundamentally the same relations hold as for MBT. Here also is seen a well defined induction period of the acceleration which increases markedly with decreasing temperature and at 120° C clearly exceeds the 1000 minute period of observation. This means that under these conditions and at this temperature, no acceleration is noticeable. It should be noted that thermal vulcanization proceeds without modification until the end of the induction period at which point the accelerated process starts suddenly every time.

The limiting value of the equilibrium swelling $1/Q_\infty$ (final value for the crosslinking), which is obtained in Figure 6 by plotting the log of $1/Q_t$ against the reciprocal vulcanization time and extrapolation of the curves to $1/t = 0$, has a value which is independent of temperature. This is quite clear for the curves for 130° C and higher, and it is not reasonable to think that the curves for 120° and 125° C would reach any other end point. A value of 0.28 was found for $1/Q_\infty$ in this case which is only a little higher than the value of 0.25 which was found in the case of pure thermal vulcanization. Therefore we con-

clude that MBTS is not a vulcanizing agent, but serves merely as an accelerator of thermal vulcanization. This can, of course, be recognized only when the final value for the vulcanization is determined by means of the limiting value of the equilibrium swelling; otherwise we may be deluded by an apparent vulcanizing action. Finally, the time law followed by the vulcanization can be derived only from its end value. In this connection, it is seen that straight lines are obtained when values of $1/(1/Q_\infty - 1/Q_t)$ are plotted against the reaction time, as in Figure 7. This also shows clearly the induction periods.

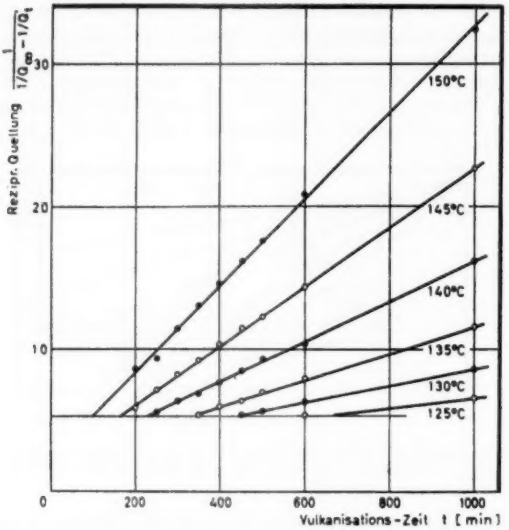

FIG. 7.—Therma vulcanization of Perbunan accelerated with MBTS plotted as a second order process at various temperatures. Ordinate: Reciprocal swelling, $\frac{1}{(1/Q_\infty - 1/Q_t)}$. Abscissa: Vulcanization time, t (min).

By plotting the rate constants calculated from the slopes of the curves of Figure 7 against the reciprocal of the absolute temperature, we get the straight line II of Figure 3. The activation energy calculated from its slope is found to be 27.1 kcal/mole, which is, accordingly, somewhat higher than the value for pure thermal vulcanization.

MBT is formed during thermal vulcanization in the presence of MBTS. Figure 8 shows the increase in MBT formation (ordinate: MBT in per cent of the initial amount of MBTS; abscissa: vulcanization time t in minutes). At lower temperatures we note a deviation from the otherwise smooth arc of the curves. This is connected with the induction period in the acceleration in the presence of MBTS (compare Figures 5 and 7). Anyone familiar with such curves will also notice that a limiting value is approached for the amount of MBT formed which is independent of the temperature. This is clearly shown in Figure 9 (ordinate: log of the MBT content in per cent of the initial MBTS; abscissa: reciprocal of the reaction time). In the case of the amount of MBTS here used (3.325 g = 0.01 mole) the amount of MBTS changed into MBT is 60

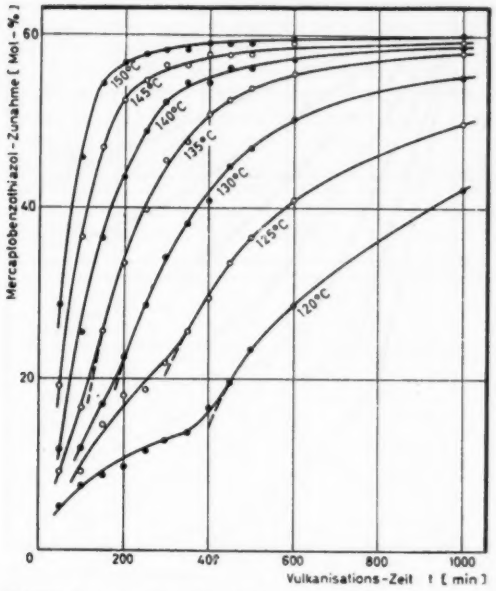

FIG. 8.—Rate of MBT increase in thermal vulcanizations of Perbunan accelerated with MBTS, at various temperatures. (MBT is in mole % of the MBTS used.) Ordinate: Mercaptobenzothiazole increase, mole %. Abscissa: Vulcanization time, t (min).

mole %, and this is independent of temperature. When the differences between the limiting value and the amounts actually transformed are plotted on a logarithmic scale against the vulcanization times, then as is shown in Figure 10,

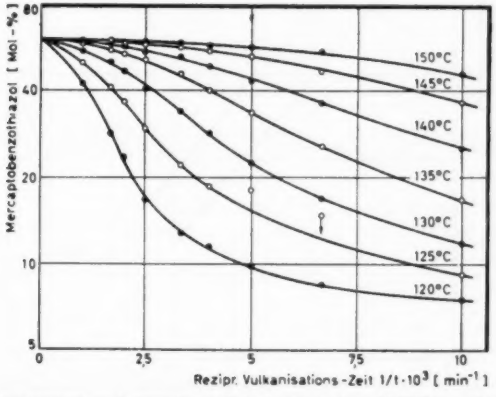

FIG. 9.—Showing temperature independence of the limiting value of MBT formed in thermal vulcanization of Perbunan accelerated with MBTS. Ordinate: Mercaptobenzothiazole, mole %. Abscissa: Reciprocal vulcanization time, $1/t \times 10^3$ (min^{-1}).

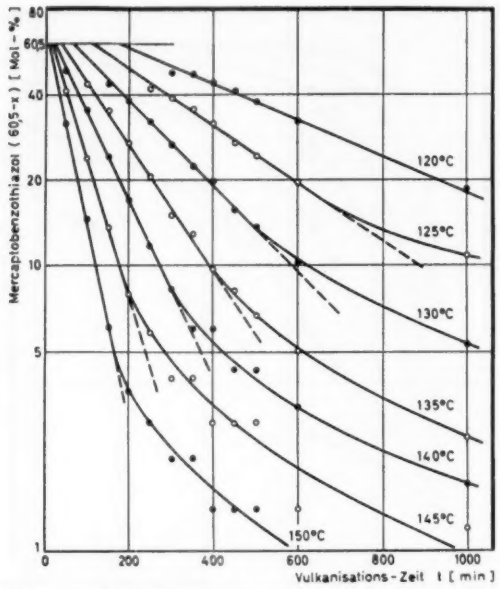

FIG. 10.—MBT formation as a first order reaction in thermal vulcanization of Perbunan accelerated with MBTS. Ordinate: Mercaptobenzothiazole (60.5-x) mole %. Abscissa: Vulcanization time, t (min).

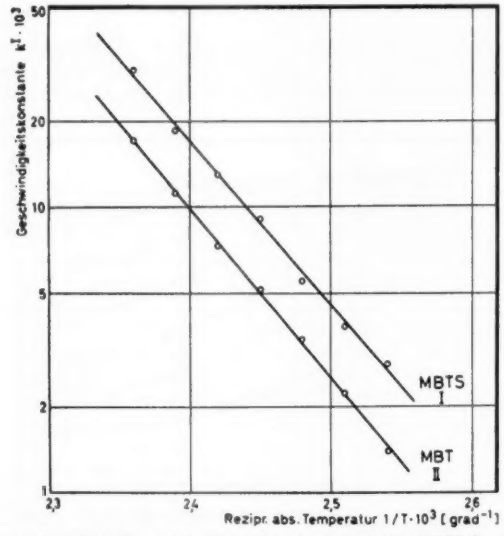

FIG. 11.—Temperature dependence of the first order rate constants for MBTS decrease (I) and MBT increase (II) in thermal vulcanization of Perbunan accelerated with MBTS. Ordinate: Rate constant, $k^I \times 10^3$. Abscissa: Reciprocal absolute temperature $1/T \times 10^3$ (degree^{-1}).

straight lines are obtained over the greater part of the reaction region, thus indicating a first order reaction for the formation of MBT.

An activation energy of 27.2 kcal/mole is derived from Curve II of Figure 11 which shows the temperature dependence of the rate constants ($\log k_{MBT} = f(1/T)$). This is in good agreement with the activation energy of crosslinking (compare Figure 3, Curve II).

Naturally, the formation of MBT corresponds to a reduction in the MBTS content and this is found to drop to zero. From this we must reason that all of the MBTS does not merely change over to MBT, but that a part of it is bound in the form of fragments by the Perbunan. Attention has already been

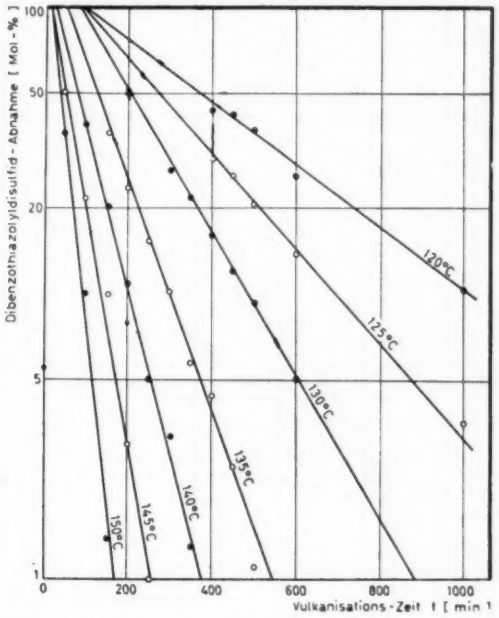

FIG. 12.—Decrease of the MBTS content as a first order reaction in thermal vulcanization of Perbunan accelerated with MBTS. Ordinate: Benzothiazolyl disulfide decrease (mole %). Abscissa: Vulcanization time, t (min).

called to this by Dogadkin[4]. Figure 12 shows that the decrease in MBTS also follows a first order reaction law. It runs more rapidly than the increase in MBT as is shown by calculations of the rate constants, but the dependence on temperature yields practically the same activation energy as is found for MBT formation, namely 26.3 kcal/mole (see Curve I in Figure II).

Valuable insight into the action of MBTS is gained by a study of the relations which hold when various starting amounts of MBTS are used. The experiments were made at 150° C.

We first found that the limiting value of the reciprocal of the equilibrium swelling, $1/Q_\infty$—not demonstrated here—is just as independent of the initial amount of MBTS as it is of the temperature, for $1/Q_\infty$ was again found to be

equal to 0.28. From this we can see that MBTS is not a vulcanizing agent for Perbunan, but acts as an accelerator of thermal vulcanization.

The crosslinking which takes place with various starting amounts of MBTS is always a second order process, as is shown in Figure 13, in which straight lines are obtained by plotting $1/(1/Q_\infty - 1/Q_t)$ against reaction time. The increasing slope of these curves with increase in the starting amounts of MBTS, in the order from *b* to *f* shows the strong acceleration of pure thermal vulcaniza-

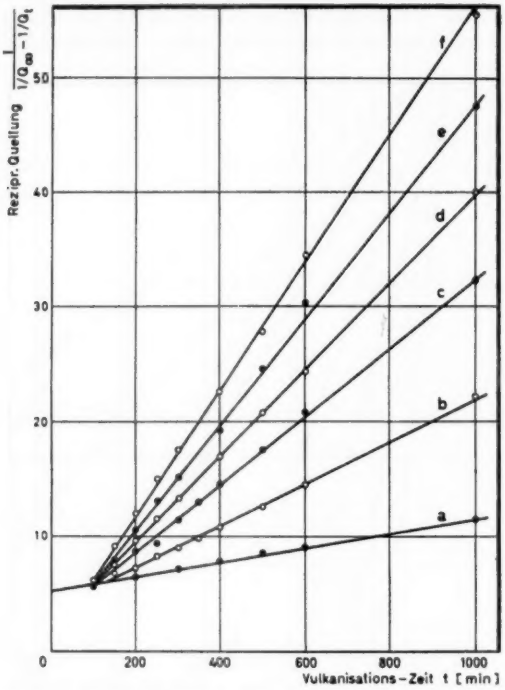

FIG. 13.—Thermal vulcanization of Perbunan as a second order reaction with various starting concentrations of MBTS and at 150° C. Curve *a*, pure thermal vulcanization; *b*, with 5 millimoles MBTS per 100 grams of rubber compound; *c*, with 10; *d*, with 15; *e*, with 2; and *f*, with 25. Ordinate: Reciprocal swelling $\frac{1}{(1/Q_\infty - 1/Q_t)}$. Abscissa: Vulcanization time, *t* (min).

tion represented by Curve *a*. The process is distinguished by a considerable induction period, which is very slightly reduced by increase in the MBTS content.

The limiting value of MBT formation is dependent upon the starting amount of MBTS, and shows an appreciable decrease with rising MBTS content. If the limiting value attained is made equal to 100, and the log of the difference (100—amount reacted) is plotted against time for the reaction, we find that the MBT formation follows a first order reaction during about 90% of the whole reaction range. This is shown by Curve II of Figure 14, on which the amounts reacted in all of the tests with various starting amounts of MBTS

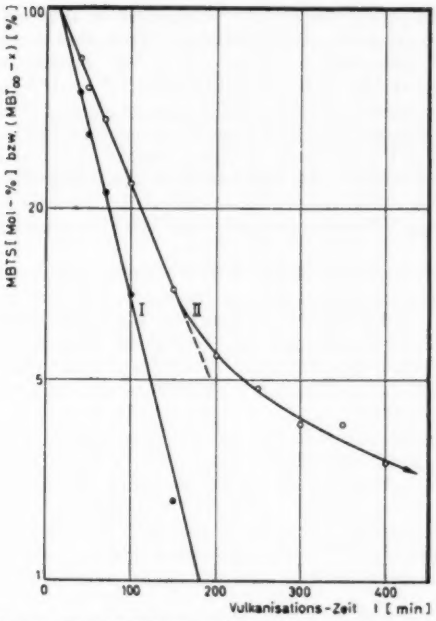

FIG. 14.—MBTS decrease (I) and MBT increase (II) as first order processes in thermal vulcanization of Perbunan accelerated with MBTS. (The points are average values of the reactions with various starting amounts of MBTS). Ordinate: MBTS (mole % or $(MBT_\infty - x)$ %). Abcissa: Vulcanization time, t (min).

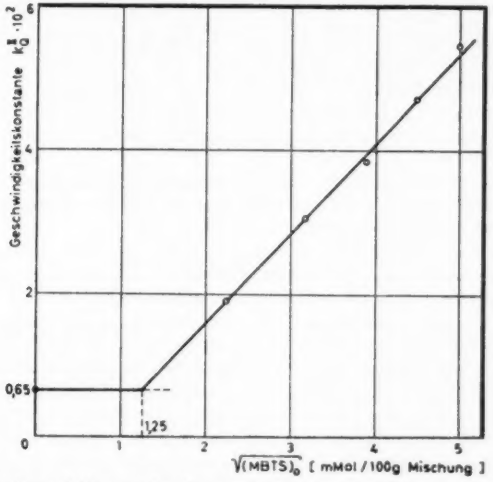

FIG. 15.—Dependence of the second order rate constant for crosslinking on the square root of the starting amount of MBTS, in thermal vulcanization of Perbunan at 150° C. Ordinate: Rate constant, $k_{II} \times 10^2$. Abcissa: $\sqrt{(MBTS)_0}$ (mmoles/100 g compound).

are brought together by this method of calculation (the points given on the curve are average values for all of the tests). From this we must conclude that the rate of MBT formation is independent of the starting amount of MBTS. The rate constant at 150° C is calculated to be 1.7×10^{-2} min^{-1}.

The values for the reduction in MBTS content show that independent of the initial amount for equal periods of time, the same fractional amount of MBTS reacts. Curve I of Figure 14 shows that a first order law is followed over the whole range of the reaction and that the reaction is independent of the starting amount of MBTS. The rate constant calculated for this reaction is $k_{MBTSI} = 2.99 \times 10^{-2}$ min^{-1}, thus showing that the MBTS disappearance is the faster reaction.

The first order reduction in the MBTS content as well as the fact that the rate of the reaction is independent of the initial MBTS content leads to the conclusion, which had already been drawn by Dogadkin, that the MBTS must undergo a homolytic decomposition. Hence the reaction must occur from a unimolecular splitting into radicals. Therefore in the case of thermal vulcanization of Perbunan accelerated by MBTS we can discuss a process induced by radicals from MBTS.

In this connection, it is worth noting—as is shown in Figure 15—that a linear relation exists between the square root of the initial concentration of MBTS and the rate constant k_{QII} of the reciprocal equilibrium swelling which defines the rate of crosslinking or of the overall reaction. This brings to mind polymerizations induced by benzoyl peroxide, azo-bis-isobutyronitrile and similar reagents, in many of which processes, a linear relation exists between the rate of the overall reaction and the square root of the concentration of catalyst.

The straight line of Figure 15 does not cut the ordinate at $k_{QII} = 0.65 \times 10^{-2}$, which is the rate constant for pure thermal vulcanization at 150° C. It does reach this value where $\sqrt{MBTS}$ is 1.25, which corresponds to a value for $(MBTS)_0$ of 1.56 mmoles. This is, obviously, the amount of MBTS which is required for some yet unknown reaction during the induction period, and if it is not equalled or exceeded no acceleration will take place. If we therefore correct the starting amounts of MBTS as well as the corresponding millimolar limiting values of the MBT which is formed assuming it is true that MBTS goes exclusively to MBT during the induction period, then, it is seen that in every case 50 mole % of MBTS goes over to MBT, and this is in agreement with results obtained by Dogadkin[4]. These results should not be considered as accidental, and they make it seem probable that an MBT molecule forms for every MBTS radical that is bound.

Dogadkin[4] has established a series of entirely plausible reactions of MBTS with the structural units of synthetic rubber. He has formulated and discussed linkage possibilities of the primary radicals thus formed while drawing on results of his work with Buna. He was taken account of the fact that part of the MBTS goes over to MBT and part is bound in the form of molecular fragments. In our opinion we must consider which of the postulated reactions would be in best agreement with the kinetic results. It must be kept in mind that we must explain the independence of the reciprocal limiting equilibrium swelling on both temperature and original MBTS content. The dependence of the rate of crosslinking (which should correspond to the overall reaction in polymerization) upon the square root of the initial MBTS content must be brought into accord with the fact that the crosslinking proceeds as a second order reaction.

We will take up these problems shortly when we report on the sulfur vulcanization of Perbunan accelerated with MBTS.

SUMMARY

In this work, the kinetics of the thermal vulcanization of Perbunan were studied with and without additives. The following results were obtained:

1. The pure thermal vulcanization of Perbunan is a very slow process which obeys a second order rate law. A limiting value of the crosslinking (reciprocal limit of equilibrium swelling) is reached, which limit is independent of the temperature. The activation energy is 23.3 kcal/mole.
2. The thermal vulcanization can be inhibited by hydroquinone but not by benzoquinone.
3. The thermal vulcanization of Perbunan can be considerably accelerated by MBTS, and other materials, and the reaction also follows a second order course. The activation starts suddenly after the expiration of an induction period, which decreases with increase in temperature. The activation energy is about 27 kcal/mole.
4. In a thermal vulcanization accelerated with MBTS, a portion of the MBTS is changed over into MBT; the amount changed is independent of temperature. Perbunan takes up MBTS in the form of molecular fragments, in stable combination.
5. The reduction in MBTS (which falls to zero) and the increase in MBT follow a first order reaction and have the same activation energy which is also identical with the energy of activation of the accelerated crosslinking. The formation of MBT is the slower of the two reactions.
6. The rate constants for the decrease in MBTS and for the increase in MBT are independent of the starting amount of MBTS, and hence we consider that this is a unimolecular process (homolysis).
7. The rate constant for the second order crosslinking reaction increases with the square root of the initial benzothiazolyl disulfide content.
8. It is indicated that the above data must be explained, with the aid of experience in the realm of polymerization kinetics. The investigations are being continued.

ACKNOWLEDGMENT

The work herein described was carried on with support from Farbenfabriken Bayer A.-G. Leverkusen, who provided the greater portion of the Perbunan and solvents without cost. We extend our sincere appreciation for this assistance.

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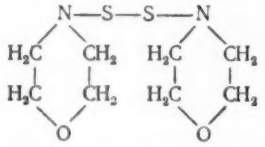
[9] See Küchler, B. L., Reference 5, p. 137.

THE ACTION OF SOME HETEROCYCLIC DISULFIDES AS AGENTS AND ACCELERATORS OF VULCANIZATION *

B. A. Dogadkin, M. S. Feldstein, I. I. Eitington, and D. M. Pevzner

The possibility of using the organic disulfides and polysulfides as agents of vulcanization has repeatedly attracted the attention of researchers[1,2]. The search centered around the polysulfides which on decomposition at the vulcanization temperatures liberate free sulfur, yet are safe at processing temperatures thereby eliminating the possibility of scorching. This article reports the characteristic action of heterocyclic disulfides the molecules of which contain =N—S—S—N= linkages. The main object of the research was the N,N′-dithiodimorpholine (DTM).



The synthesis of DTM was carried out by working up morpholine with sulfur chloride in dichloroethane solution at the temperature of 2–4° C in the presence of an alkali. After boiling off dichloroethane, the reaction product, crystallized from ethyl alcohol, had a melting point of 124–126° C and analyzed as follows:

	C	H	N	S
For $C_8H_{16}O_2N_2S_2$:				
Calculated per cent	40.67	6.78	11.88	27.11
Actual per cent	40.46	7.05	12.19	26.96

The analytical data show that the obtained product was pure DTM.

The vulcanizing ability of DTM was tested in gum and filled stocks of SBR type synthetic rubber (SKS-30 A) which did not contain elemental sulfur. 7.4 phr of DTM were used which is equivalent to 2.0 phr of sulfur ordinarily used in rubber compounds in the presence of accelerators. A sulfur containing control compound was studied simultaneously. In order to determine the quantity of bound sulfur, cured samples were extracted with acetone for 70 hours at room temperature to remove all of the unreacted DTM and the free sulfur. Figure 1 shows the kinetics of reaction of sulfur with the raw rubber at 143° C.

As seen from Figure 1, DTM causes a considerably faster reaction of sulfur with the raw rubber as compared to a compound containing elemental sulfur without any accelerators. DTM also causes a considerable crosslinking of

* Translated by Theodore Shevzov for Rubber Chemistry & Technology, from *Kauchuk i Rezina* 17, No. 9, 7–12 (1958).

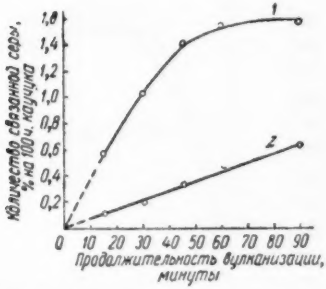


FIG. 1.—Kinetics of reaction of sulfur (in channel black compounds) using N,N′-dithiodimorpholine (*1*) and sulfur (*2*) as curing agents. Abscissa; curing time, minutes. Ordinate; phr combined sulfur.

rubber as can be seen from per cent swelling of vulcanizates in xylene shown in Figure 2.

Data presented in Figure 3 shows that sulfur alone does not give normal (useful) vulcanizates after 120 min cure while DTM gives good cures after 45 min of curing. Tensile strength values of optimum cures with DTM are quite comparable to those with sulfur plus the accelerator, benzothiazolyl diethylsulfenamide (sulfenamide BT).

The action of DTM in sulfur containing compounds is shown in Figure 4-A. As compared to sulfenamide BT, DTM effects less crosslinking judging by the developed modulus. However the activity of the DTM is sharply increased by the addition of small amounts (0.3–0.5 phr) of MBT or sulfenamide BT. Using DTM in combination with these accelerators results in such effective curing systems that it is possible not only to cut down the sulfur but eliminate it completely from the compound. Data in Figure 4-B show that the curing system based on DTM and dibenzothiazolyldisulfide (MBTS) (without sulfur)

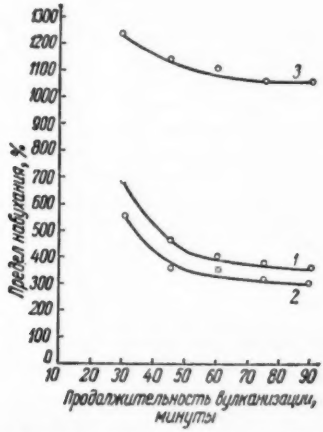


FIG. 2.—Variations in degree of swelling of vulcanizates containing N,N′-dithiodimorpholine (*1*), N,N′-dithiodipiperidine (*2*), and sulfur (*3*). Abscissa; curing time, minutes. Ordinate; % swelling in xylene.

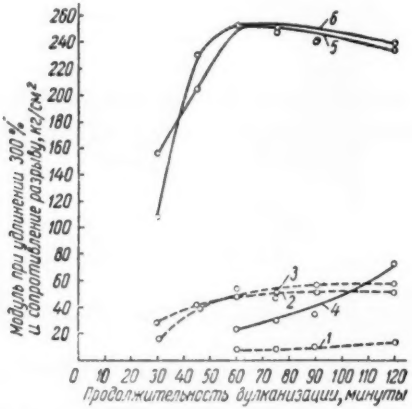


FIG. 3.—Tensile data of compounds filled with channel black: *1, 2, 3*—modulus; *4, 5, 6*—tensile at break; *1, 4*—5.0 phr of sulfur; *2, 5*—7.4 phr of N,N′-dithiodimorpholine; *3, 6*—2.0 phr sulfur and 1.0 phr sulfenamide BT. Abscissa; curing time, minutes. Ordinate; modulus at 300% elongation and tensile at break, kg/cm².

at optimum cure (40–50 min at 138° C) gives vulcanizates with moduli equivalent to those obtained with sulfur (3.0 phr) and sulfenamide BT.

It should be noted at this point that within the first 30 minutes of curing time the DTM containing compounds have a slower rate of cure than the compounds containing sulfur and sulfenamide BT. This property of the DTM curing systems decreases the tendency toward premature vulcanization during the high processing temperatures of the DTM containing raw stock. Thus, at 110° C, as seen from the Mooney scorch curves (Figure 5), DTM compounds as well as the sulfur–sulfenamide BT systems do not exhibit any tendency to-

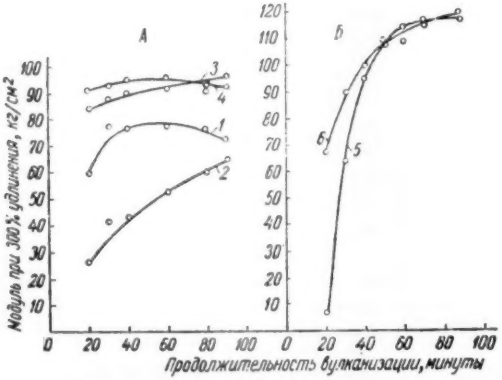


FIG. 4.—Effectiveness of N,N′-dithiodimorpholine in sulfur compounds containing furnace black (A), and in breaker-type compounds (B): *1*—2.0 phr sulfur and 1.2 phr sulfenamide BT; *2*—1.5 phr sulfur and 1.5 phr N,N′-dithiodimorpholine; *3*—1.5 phr sulfur, 1.5 phr N,N′-dithiodimorpholine and 0.5 phr MBT; *4*—1.5 phr sulfur, 1.5 phr N,N′-dithiodimorpholine and 0.5 phr sulfenamide BT; *5*—3.7 phr N,N′-dithiodimorpholine and 1.0 phr MBTS; *6*—3.0 phr sulfur and 1.0 phr sulfenamide BT. Abscissa; curing time, minutes. Ordinate; modulus at 300% elongation, kg/cm².

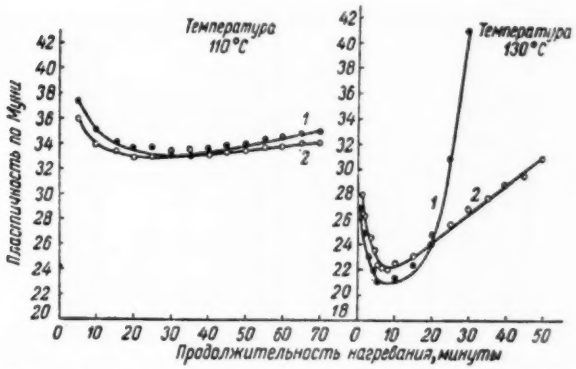


FIG. 5.—The rate of change of Mooney viscosity of the breaker-type compounds: *1*—3.0 phr sulfur and 1.0 phr sulfenamide BT; *2*—3.7 phr N,N′-dithiodimorpholine and 1.0 phr MBTS. Abscissa; time, minutes. Ordinate; Mooney viscosity.

ward scorching. However, at 130° C the Mooney scorch curve of the sulfur-sulfenamide system rises abruptly while the DTM system exhibits a much more gradually rising curve (Figure 5). Thus, the compounds containing DTM (with the MBTS accelerator) vulcanize quite rapidly above 130° C.

The same is shown by the data in Table I. Table I shows the degree of swelling in xylene and solubility in chloroform of the vulcanizates which were cured for 60 minutes at 100° C, 110° C, 120° C, and 130° C.

The curing action, of the DTM curing system, as described above, makes it possible to retain the thermoplasticity of the compound in the initial stages of vulcanization for a longer period of time as compared to a conventional sulfur plus an accelerator system. This condition and the absence of the free sulfur and consequently the absence of sulfur bloom on the surface of the uncured compound should improve the uniformity of the multilayer products[3]. The dynamic strength at the interface of the laminate consisting of the tread-breaker-tread system was tested by the method based on the deformation caused by the multistage shear[4]. The curing systems of the tread and breaker compounds were designed to give approximately the same modulus values. As may be seen from the data in Figure 6 the DTM curing system gives significantly better bond strength in the laminated systems.

Thus, by substituting the sulfur curing system with the DTM system the dynamic endurance of the laminated system is increased from 1000 to 1700 cycles. DTM also has a favorable effect on cut growth resistance at multiple

TABLE I

THE DEGREE OF SWELLING IN XYLENE AND SOLUBILITY IN CHLOROFORM AT VARIOUS CURING TEMPERATURES

	Curing temperatures							
	100°	110°	120°	130°	100°	110°	120°	130°
Curing agents	% swelling in xylene				% solubility in chloroform			
N,N′-Dithiodimorpholine 7.4 phr	1085	1100	1045	975	61.2	60.4	55.0	47.5
Sulfur (2.0 phr) sulfenamide BT (1.0 phr)	980	950	860	670	63.2	59.8	49.5	22.5

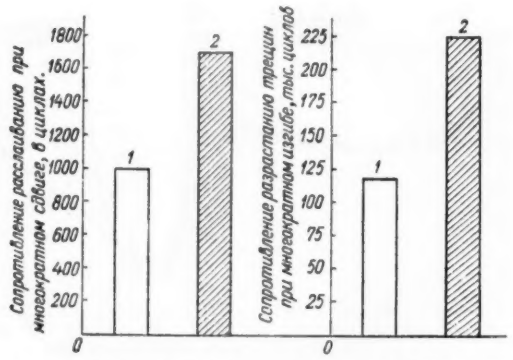
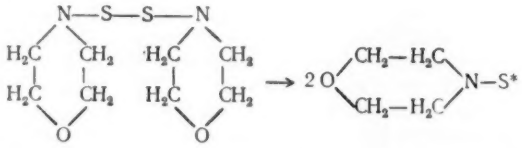


FIG. 6.—The effect of N,N′-dithiodimorpholine on the endurance of vulcanizates subjected to the multistage deformation. *1*—sulfur, sulfenamide BT; *2*—N,N′-dithiodimorpholine, MBTS. Ordinate (at left); resistance to delamination, cycles. Ordinate (at right); cut growth (multistage deflection) thousands of cycles.

deformation. The improvement in fatigue resistance obtained by using the DTM is apparently due to the presence of stable vulcanizing bonds.

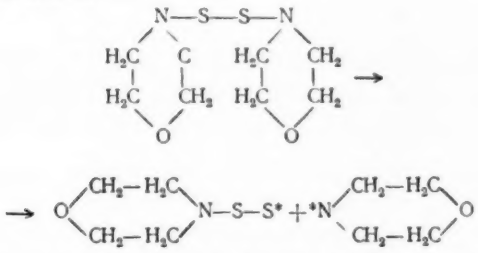
Thus, the presented data show that the use of heterocyclic disulfides, particularly DTM, leads to an improvement of the number of important physical properties of the vulcanizates. These curing systems vulcanize the stock at higher temperatures and consequently widen the range of possible processing temperatures. The economic feasibility of using these systems will depend largely on the possibility of using smaller amounts of these materials. Therefore, it appears expedient to continue the work of finding activators which would enable us to use DTM in amounts conventionally employed for vulcanization accelerators.

The vulcanizing action of DTM could be the result of its decomposition to free radicals at the S—S bond:

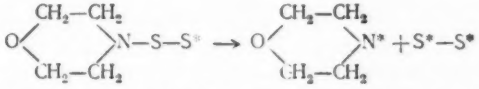


and the subsequent interaction between these radicals and the rubber hydrocarbon chain according to the mechanism which we have described for MBTS and benzothiazolesulfendiethylamide[5,6]. In that case, the vulcanization process should yield structures which should have the same sulfur and nitrogen content as the thiomorpholine radical. In order to verify this, variations in the so called "true" free sulfur content in the process of vulcanization were examined. The "true" free sulfur content was determined by the Shulte[7] method on DTM vulcanizates prior to acetone extraction. As seen from Figure 7, during the process of vulcanization both sulfur and nitrogen combine with the rubber. The curves show progressive increase in combined sulfur and nitrogen with increase in curing time and also that considerably more sulfur than nitrogen combines with the rubber.

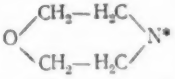
The excess in combined sulfur shows that DTM also decomposes according to the following scheme:



This decomposition may eventually lead to the liberation of "free" sulfur in the form of a biradical:



The liberation of this "free" sulfur and its interaction with rubber are reflected in Curve *3* (Figure 7). The radicals



interact with rubber to a lesser extent, apparently because they combine with each other.

The presence of the maximum (Curve *3*, Figure 7) is explained by the fact that in the initial stages of vulcanization the decomposition of DTM is more rapid than the reaction between sulfur and rubber.

In order to determine whether such vulcanizing action is characteristic of

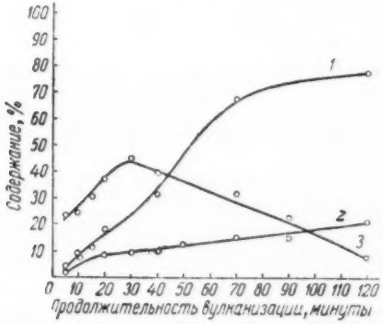


FIG. 7.—Kinetics of reaction of sulfur and nitrogen during vulcanization of unfilled compounds with N,N'-dithiodimorpholine. *1*—combined sulfur content $\frac{\text{S combined}}{\text{S total}}$ per cent; *2*—combined nitrogen content $\frac{\text{N combined}}{\text{N total}}$ per cent; *3*—true free sulfur content $\frac{\text{S free}}{\text{S total}}$ per cent. Abscissa; curing time, minutes. Ordinate; content, per cent.

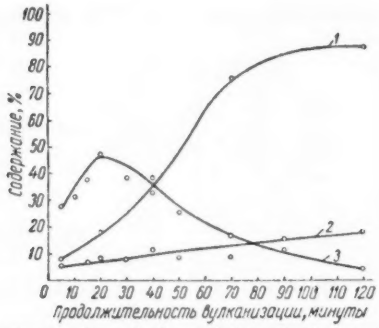
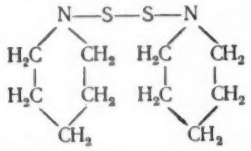


FIG. 8.—Kinetics of reaction of sulfur and nitrogen during vulvanization of unfilled compounds with N,N′-dithiodipiperidine: *1*—combined sulfur content $\frac{\text{S combined}}{\text{S total}}$ per cent; *2*—combined nitrogen content $\frac{\text{N combined}}{\text{N total}}$ per cent; *3*—true free sulfur content $\frac{\text{S true}}{\text{S total}}$ per cent. Abscissa; curing time, minutes. Ordinate; content, per cent.

DTM or whether it is inherent with other heterocyclic compounds containing =N—S—S—N= bonds, the vulcanizing activity of N,N′-dithiodipiperidine



(DTP) was also investigated.

DTP was obtained by working up piperidine with sulfur chloride in ether solution[8] at −10° C and subsequent crystallization from alcohol. The reaction product (m.p. 63–64° C) analyzed as follows:

	C	H	N	S
For $C_{10}H_{20}S_2N_2$:				
Calculated per cent	51.72	8.62	12.07	27.58
Actual per cent	51.60	8.64	11.38	27.51

The analytical data show the high purity of the obtained DTP.

As seen from Figure 2, the crosslinking effect of DTP is stronger than that of DTM. Data showing the kinetics of reaction of sulfur and nitrogen and the liberation of free sulfur during vulcanization of rubber with DTP are shown in Figure 8.

The characteristics of the curves obtained for DTP vulcanizates are similar to those obtained with DTM. Evidently, the vulcanizing action of this type of compounds is a result of breakdown to free radicals with subsequent interaction of these radicals with the molecular chains of rubber.

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[2] Sibley R., RUBBER CHEM. & TECHNOL. **24**, No. 1, 211 (1951).
[3] Dogadkin, B., Feldstein M., and Pevzner, D., Proceedings of the conference, "Adhesive Strength Between the Elements of the Multi-Layer Rubber Goods", p. 118, Goskhimizdat (1956).
[4] Kaznikovsky, M., Proceedings of the conference, "Adhesive Strength Between the Elements of the Multi-Layer Rubber Goods", p. 166, Goskhimizdat (1956).
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[6] Dogadkin B., Feldstein M., and Pevzner D., *Zhurnal Prikladnoi Khimii* **28**, 5, 533 (1955).
[7] Dymov A., "Technical Analysis of Ores and Metals", Gostekhizdat (1949).
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DERIVATIVES OF 2-MERCAPTOBENZOTHIAZOLE AND DIMETHYLDITHIOCARBAMIC ACID AS VULCANIZATION ACCELERATORS *

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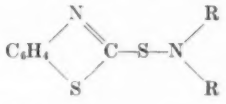
The relation between the activity of an accelerator and its chemical structure is of considerable interest because the explanation of such relations will, to a certain extent, elucidate the mechanism of accelerator action and determine the ways in which stocks with predetermined curing properties can be obtained. There are very few references in the literature devoted to the systematic analysis of this problem. We would mention the work of Harman[1] concerning the determination of the effect of certain derivatives of 2-mercaptobenzothiazole on the efficiency of vulcanizing natural rubber, as well as the work of Mathes[2] on the activity of various mercaptobenzothiazole derivatives in their role as accelerators for natural rubber–synthetic rubber blends.

In previous investigations[3,4], we have determined the effect of the chemical structures of a series of sulfenamide compounds on vulcanizing activity. In particular, it has been determined that the kinetics of vulcanization of styrene-butadiene rubber stocks, in the presence of sulfenamide derivatives of 2-mercaptobenzothiazole, are characterized by the presence of an induction period (scorch period), the duration of which depends, to a significant extent, upon the nature of the radical (R) in the amino group of the accelerator molecule



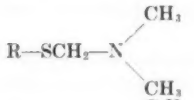
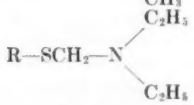
On the basis of the results obtained, the sulfenamide accelerators have been chosen from the class of derivatives of 2-mercaptobenzothiazole, and have been recommended to the rubber industry. These substances provide the basis for extremely efficient vulcanization.

The present work constitutes an extension of our previous investigations concerning the dependence of the activity of accelerators upon chemical structure. We have examined the derivatives of 2-mercaptobenzothiazole in which the thiol hydrogen is replaced by the nonpolar methyl radical, as well as compounds in which the hydrogens of this methyl radical are further replaced by various functional groups. The compounds which were synthesized and investigated are presented in Table I. The activity of these compounds has been estimated from the kinetics of sulfur combination, the change in modulus and tensile strength in stocks of natural and styrene-butadiene (SKS-30AM) rubbers at the vulcanization temperature of 143°. 2-Mercaptobenzothiazole (MBT) served as

* Translated for Rubber Chemistry and Technology by A. D. Keneth and M. A. Golub from *Kauchuk i Rezina*, No. 1, pages 16–21 (1959).

TABLE I

STRUCTURES INVESTIGATED

Formula	Name of compound
I. Derivatives of 2-mercaptobenzothiazole*	
R—SH	2-Mercaptobenzothiazole
R—SCH_3	Methyl-2-thiolbenzothiazole
R—SCH_2OH	Hydroxymethyl-2-thiolbenzothiazole
R—SCH_2CH_2OH	Hydroxyethyl-2-thiolbenzothiazole
R—SCH_2COOH	Carboxymethyl-2-thiolbenzothiazole
R—$SCH_2COOC_2H_5$	Ethyl ester of carboxymethyl-2-thiolbenzothiazole
$[R—SCH_2COO]_2Zn$	Zinc salt of carboxymethyl-2-thiolbenzothiazole
	Dimethylaminomethyl-2-thiolbenzothiazole
	Diethylaminomethyl-2-thiolbenzothiazole or benzothiazolyl-2-thiolmethyldiethylamine
II. Derivatives of dimethyldithiocarbamic acid	
$(CH_3)_2N—C(S)—SCH_3$	Methyl dimethyldithiocarbamate
$(CH_3)_2N—C(S)—SCH_2OH$	Hydroxymethyl dimethyldithiocarbamate
$(CH_3)_2N—C(S)—SCH_2COOH$	Carboxymethyl dimethyldithiocarbamate
$[(CH_3)_2N—C(S)—SCH_2COO]_2Zn$	Zinc salt of carboxymethyl dimethyldithiocarbamate
$(CH_3)_2N—C(S)—SCH_2COOC_2H_5$	Ethyl ester carboxymethyl dimethyldithiocarbamic acid
$(CH_3)_2N—C(S)—SCH_2N(CH_3)_2$	Dimethylaminomethyl dimethyldithiocarbamate
$(C_2H_5)_2N—C(S)—SCH_2N(C_2H_5)_2$	Diethylaminomethyl dimethyldithiocarbamate

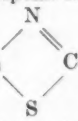
* R in the structures above stands for C_6H_4( )—. See footnote, p. 985.

the control. In SKS stocks for comparison, data were obtained which indicate that 2-benzothiazolylsulfen-N,N-diethyl amide (sulfenamide BT) is one of the most efficient vulcanization accelerators for this type of rubber. The recipes of the control stocks selected are given in Table II. For work with the various

TABLE II

RECIPES OF THE STOCKS, PHR

Ingredients / No. of stock	1	2	3	4	5
Natural rubber (smoked sheet)	100	100	—	—	—
SKS-30AM (plasticity 0.5)	—	—	100	100	100
Sulfur	3	3	2	2	2
MBT	0.7	0.8	—	—	—
Sulfenamide BT	—	—	1.0	1.2	1.2
Zinc oxide	5	5	5	5	5
Stearic acid	0.5	2.0	2.0	2.0	2.0
Channel black	—	40	—	50	—
Furnace black	—	—	—	—	50

accelerators under investigation, they were introduced in equimolar amounts to MBT for the natural rubber stocks, and to sulfenamide BT for the SKS stocks, in place of the accelerator loadings shown in Table II. Figure 1 shows the effect of various substituents on the thiol group of MBT on the kinetics of sulfur combination with the unsaturated units in natural rubber. The substitution of the thiol hydrogen by the nonpolar methyl radical (i.e., transformation of RSH into $RSCH_3$, where R is  decreases sharply the accelerating quality of MBT. The methylol derivative $RSCH_2OH$ obtained through the introduction of the polar hydroxyl on the methyl group becomes an efficient

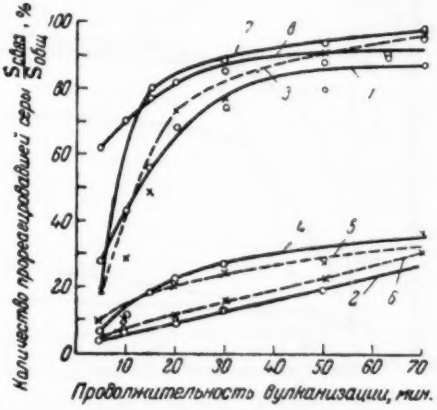


FIG. 1.—The effect of various substituents on the thiol group of MBT on the kinetics of sulfur combination with the unsaturated units in natural rubber. *1*—R-SH. *2*—$R\text{-}SCH_3$. *3*—$R\text{-}SCH_2OH$. *4*—$R\text{-}SCH_2CH_2OH$. *5*—$R\text{-}SCH_2COOH$. *6*—$R\text{-}SCH_2COOC_2H_5$. *7*—$R\text{-}SN(C_2H_5)_2$. *8*—$R\text{-}SCH_2N(C_2H_5)_2$. R is . The abscissa gives the vulcanization time in minutes; the ordinate the amount of sulfur reacted, expressed as $(S_{combined}/S_{total})\%$.

accelerator similar in activity to MBT*. On substituting the methyl group by an ethyl group (i.e., obtaining $RSCH_2CH_2OH$), the activity is sharply reduced. Replacing hydrogen in the methyl radical by the electronegative carboxyl group (forming carboxymethyl-2-thiolbenzothiazole, $RSCH_2COOH$) does not increase the activity. Similarly, blocking the carboxyl group through the formation of an ester ($RSCH_2COOC_2H_5$) or a salt ($(RSCH_2COO)_2Zn$) practically brings about no increase in the vulcanizing activity.

Analogous results are observed for SKS stocks. These are clearly seen both from the data for the kinetics of introducing sulfur into the polymer chains (Figure 2) and the data for the change in a significant index (in particular, the modulus) of the rubber stocks in the course of vulcanization (Figure 3).

* Editor's note: Contrary to the text it is usually considered that the methylol derivative of MBT has the methylol group on the nitrogen atom and not on the sulfur. Indeed, the location of the "extra" hydrogen atom in MBT is, apparently, open to some question.

The activity of methyl-2-thiolbenzothiazole increases substantially on replacing hydrogen in the methyl radical by an amine group, i.e., when using benzothiazolyl-2-thiolmethylenediethylamine ($R—SCH_2N<^{C_2H_5}_{C_2H_5}$). This accelerator (BTMA) substantially surpasses MBT in activity and is practically equal to sulfenamide BT in efficiency[5]. With respect to this particular point, this accelerator was studied more closely. Shown below are data characterizing the action of technical BTMA in stocks containing various ingredients, as well as data on the effect of this accelerator on the properties of the vulcanizate.

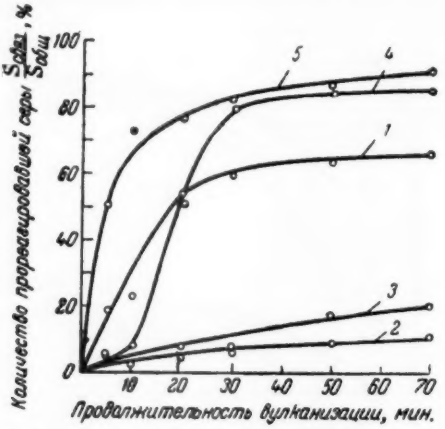


FIG. 2.—The kinetics of sulfur combination during the vulcanization of the unsaturated groups of butadiene-styrene rubber (SKS-30A). *1*—R-SH. *2*—R-SCH_3. *3*—R-$SCH_2COOC_2H_5$. *4*—R-$SN(C_2H_5)_2$. *5*—R-$SCH_2N(C_2H_5)_2$. The abscissa gives the vulcanization time in minutes; the ordinate the amount of sulfur reacted, expressed as $(S_{combindd}/S_{total})\%$.

The efficiency of the accelerator BTMA in stocks of natural rubber containing channel black is demonstrated in Figure 4. In these stocks BTMA surpasses MBT extensively in activity and affords vulcanizates which are comparable in tensile strength to vulcanizates obtained through the use of sulfenamide BT, but which are somewhat inferior to the latter in modulus characteristics. In SKS stocks (Figure 5) BTMA in the presence of channel black causes a structuring effect which is equal to the activity of sulfenamide BT, while in the presence of furnace black it surpasses the activity of this accelerator.

The kinetics of vulcanization of stocks containing benzothiazolyl-2-thiolmethyldiethylamine have the distinctive feature compared to stocks with sulfenamide BT in that the former accelerator produces a high rate of vulcanization in the first stage of the process (Figures 1 and 2). Such action of BTMA could result in scorching. The effect of this accelerator on the viscoelastic properties of rubber stocks has been investigated in oil-extended SKS stocks (SKS-30AM15), the rubber being of the unprotected type. In such stocks the sulfenamide BT is generally used along with MBTS; this is why MBTS was introduced together with BTMA in the stocks investigated.

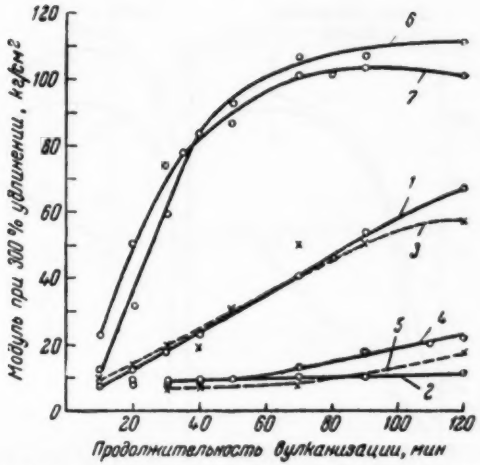


FIG. 3.—The kinetics of the change in the modulus during vulcanization of SKS-30AM stocks containing channel black. *1*—R-SH. *2*—R-SCH_3. *3*—R-SCH_2OH. *4*—R-SCH_2CH_2OH. *5*—R-SCH_2COOH. *6*—R-$SN(C_2H_5)_2$. *7*—R-$SCH_2N(C_2H_5)_2$. The abscissa gives the vulcanization time in minutes; the ordinate the modulus at 300% elongation, kg/cm².

From data obtained on the Goodrich plastometer at 110° (Figure 6), no differences of any importance whatsoever have been discovered between the action of sulfenamide BT and that of the accelerator BTMA.

Plasticity measurements on the Mooney machine at 125° point out that stocks containing the accelerator BTMA have a greater tendency towards premature vulcanization. However, the latter can be easily eliminated by the

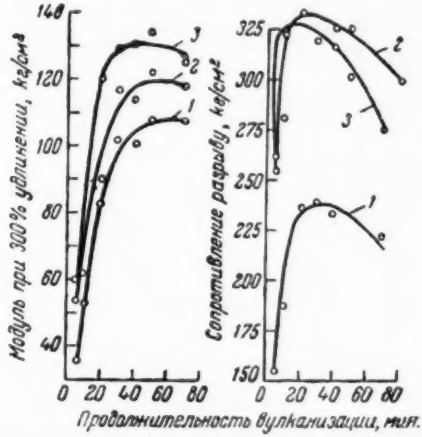


FIG. 4.—The effect of accelerator BTMA in natural rubber stocks containing channel black. *1*—MBT, 0.8 phr. *2*—Accelerator BTMA, 1.0 phr. *3*—Sulfenamide BT, 1.0 phr. The abscissa gives the vulcanization time in minutes; the left hand ordinate the modulus at 300% elongation, kg/cm² and the right hand ordinate the tensile strength, kg/cm².

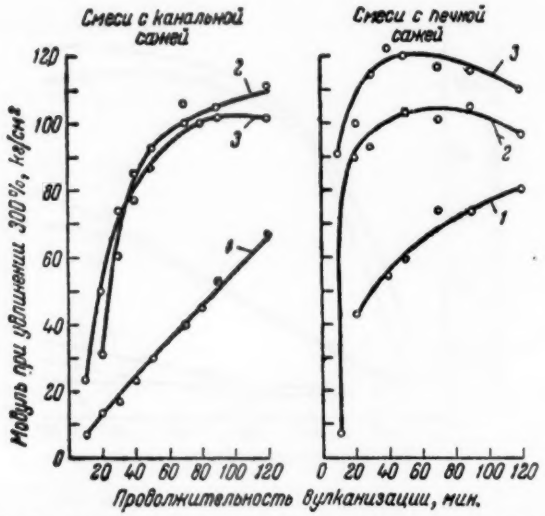


FIG. 5.—The effect of accelerator BTMA in oil-extended butadiene-styrene rubber stocks (8KS-30AM). *1*—MBT, 0.84 phr. *2*—Sulfenamide BT, 1.2 phr. *3*—Accelerator BTMA, 1.27 phr. The abscissa gives the vulcanization time in minutes; the ordinate the modulus to 300% elongation, kg/cm². The left hand graph depicts results for blends with channel black; the right hand graph blends with furnace black.

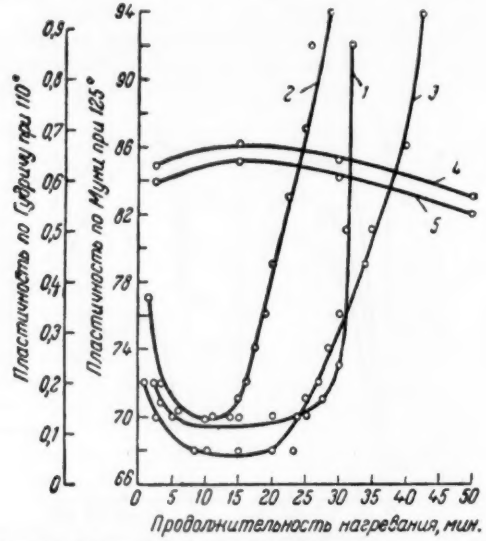


FIG. 6.—The dynamics of change of plasticity of SKS-30AM stocks of the unprotected type. *1, 2, 3*—Data obtained on the Mooney plastometer. *4, 5*—Data obtained on the Goodrich plastometer. *1, 4*—Sulfenamide BT. *2, 5*—Accelerator BTMA. *3*—Accelerator BTMA plus 0.3 phr phthalic anhydride. The abscissa gives the time of heating in minutes; the left hand ordinate the Goodrich plasticity at 110° and the right hand ordinate the Mooney plasticity at 125°.

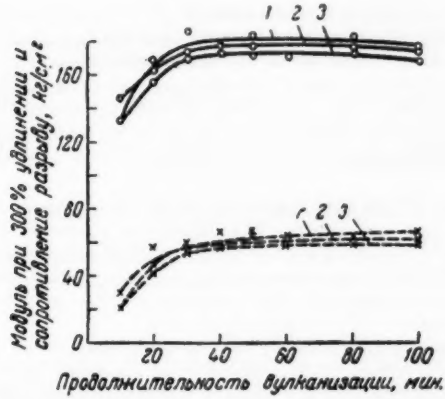


FIG. 7.—The effect of accelerator BTMA in SKS-30AM stocks of the protected type. – – – – – Modulus. ——— Tensile strength. *1*—Sulfenamide BT, 1.1 phr, Altax, 0.3 phr. *2*—Accelerator BTMA, 1.2 phr, MBTS, 0.3 phr. *3*—Sulfenamide Z (Santocure), 1.2 phr, MBTS, 0.3 phr. The abscissa gives the time of vulcanization in minutes; the ordinate the modulus at 300% elongation and the tensile strength, kg/cm².

introduction of small (0.3 phr) amounts of phthalic anhydride (Curve *3*, Figure 6). Phthalic anhydride is extremely efficient as a retarder (in the early stage of the process) compared to BTMA alone. The use of phthalic anhydride in this case has practically no bearing on the time for achieving optimum results in vulcanization and upon the physical properties of the vulcanizates.

In SKS stocks (SKS-30AM15) of the protected type, the accelerator BTMA in combination with MBTS gives vulcanizates (Figure 7) having properties which are very similar to those of vulcanizates obtained with sulfenamide BT (or sulfenamide Z) and MBTS. A set of properties characteristic of the vulcanizates of the protected type is given in Table III. As seen from the data in this table, vulcanizates with accelerator BTMA are identical to vulcanizates

TABLE III

PHYSICAL PROPERTIES OF RUBBERS FROM SKS–30AM OF THE PROTECTED TYPE

Property	Time of vulcanization, min	Sulfenamide BT-1.1 phr; MBTS-0.3 phr	Accelerator BTMA-1.2 phr; MBTS-0.3 phr
Modulus at 300% elongation, kg/cm²	50	63.5	58.5
Tensile strength, kg/cm²	50	183	181
Tear resistance, kg/cm	50	69	73
Temperature coefficient of stability at 110°:			
Concerning tensile strength	60	0.48	0.47
Concerning elongation	—	0.71	0.79
Coefficient of aging at 100° during 120 hr			
Concerning tensile strength	60	0.93	0.94
Concerning elongation	—	0.55	0.54
Shore hardness	60	60	59
Resistance to cracking after many cycles	70	a) 73,950 b) 61,250	a) 62,500 b) 71,250
Abrasion, cm³/kilowatt-hr	70	278	263

TABLE IV

REQUIRED AMOUNTS OF MBT AND DIETHYLAMINE
(PER KG OF FINISHED PRODUCT)

Name	Accelerator BTMA (90% yield)	Sulfenamide BT (on MBT)
MBT	0.736	0.779
Diethylamine	0.353	0.738

with sulfenamide BT in tear resistance, dynamic hardness, temperature coefficient of stability and aging. The differences observed, if any, are well within the limits of the usual scatter of data. This indicates that vulcanizates obtained with BTMA in the capacity of a basic accelerator are practically the same as vulcanizates obtained with sulfenamide BT over the entire range of physical properties.

The accelerator, sulfenamide BT, widely used today in the rubber industry, is a liquid, unstable inflammable material which is applied in the form of special pastes. The accelerator BTMA has the advantage over sulfenamide BT in that it is a crystalline compound (melting point, 86–87°), stable and noninflammable and not requiring any special handling on being introduced into rubber stocks. Moreover, BTMA is much cheaper than sulfenamide BT since its production requires smaller amounts of diethylamine (Table IV). Thus, benzothiazolyl-2-thiolmethylenediethylamine as a vulcanization accelerator is of considerable practical interest.

In a similar way, by considering the accelerators derived from 2-mercaptobenzothiazole, certain derivatives of dimethydithiocarbamic acid containing

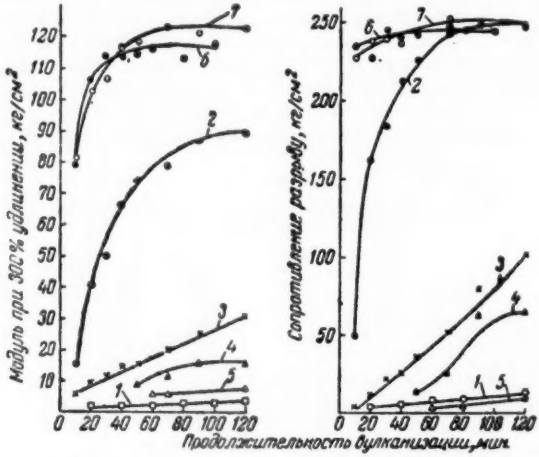


FIG. 8.—The vulcanizing activity of derivatives of dimethyldithiocarbamic acid in SKS-30AM stocks containing channel black. *1*—R-SCH_3. *2*—R-SCH_2OH. *3*—R-SCH_2CH_2OH. *4*—R-SCH_2COOH. *5*—R-$SCH_2COOC_2H_5$. *6*—R-$SCH_2N(CH_3)_2$. *7*—Thiuram where R is $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!N\!-\!C\!-\!$ ‖ S. The abscissa gives the time of vulcanization in minutes; the left-hand ordinate the modulus at 300% elongation, kg/cm² and the right hand ordinate the tensile strength, kg/cm².

analogous functional groups were synthesized and investigated. In the case where the derivatives of this acid were used, the same regularity was established for the change in activity depending on the presence of various functional groups, as was the case for the derivatives of 2-mercaptobenzothiazole (Figure 8). In particular, replacing the hydrogen of the ester methyl group in methyl dimethyldithiocarbamate by a disubstituted amine group, for example, dimethylamine, the structure of dimethylaminomethyl dimethyldithiocarbamate is obtained:

$$(CH_3)_2N—C(S)—S—CH_2—N(CH_3)_2$$

which is an exceptionally active accelerator. This structure can be used as an ultra accelerator and is known commercially[6] as "Robac DAMD".

CONCLUSIONS

1. We have synthesized and investigated as vulcanization accelerators the derivatives of 2-mercaptobenzothiazole (MBT) in which the thiol hydrogen is replaced by the nonpolar methyl radical, as well as compounds in which methyl hydrogen of the methyl derivative is replaced by various functional groups.

2. It has been shown that methyl-2-thiolbenzothiazole is not an accelerator. The replacement in this compound of one of the methyl hydrogens by a polar hydroxyl group substantially enhances the activity (see, however, editors note in the text). The substitution of hydrogen by a carboxyl group does not increase vulcanizing activity.

3. We have determined that replacement of a methyl hydrogen by an amino radical increases sharply the accelerating activity. The structure obtained as a result of this reaction, benzothiazolyl-2-thiolmethyldiethylamine (BTMA), is of great practical interest as an accelerator.

4. The accelerator BTMA in stocks of natural and SKS rubber gives vulcanizates which are substantially superior in their properties to rubbers cured with MBT, and are practically equal to vulcanizates obtained with sulfenamide accelerators—sulfenamide BT and sulfenamide Z (Santocure).

5. The accelerator BTMA is much cheaper than sulfenamide BT since its production requires much less diethylamine.

6. It has been determined that, just as in the case of 2-mercaptobenzothiazole derivatives, for the derivatives of dimethyldithiocarbamic acid containing analogous functional groups the same results are obtained for the change in activity depending upon the chemical structure of the accelerator.

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DEPENDENCE OF THE ULTIMATE PROPERTIES OF A SBR RUBBER ON STRAIN RATE AND TEMPERATURE *†

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INTRODUCTION

The tensile strength and ultimate elongation of polymeric materials depend on both the temperature and experimental time scale[1]. The mechanical properties of amorphous polymers at temperatures above their glass transition temperature T_g are more amenable to treatment in terms of molecular theories than are their mechanical properties at temperatures below T_g or the mechanical properties of crystalline polymers. For amorphous polymers at temperatures above T_g the viscoelastic properties in small deformations have been studied rather extensively[2,3], and several molecular theories—essentially identical—have been published[4–6]. In contrast, few systematic studies have been made of the effect of time and temperature on the ultimate properties. Consequently, only a limited amount of data is available which can serve as a basis for developing and verifying molecular theories dealing with ultimate properties.

A recent theory by F. Bueche[7] treats the time and temperature dependence of tensile strength. According to his theory, the tensile strength for a given material is a universal function of a reduced time or a reduced strain rate, except at short times or high strain rates where the material approaches glass-like behavior. Also, to superpose data measured at different temperatures, a shift factor is needed which is determined by the temperature dependence of the frictional factor for polymeric segment mobility and thus is the same factor as used to superpose viscoelastic data measured in small deformations. Thus, according to Bueche's theory, the temperature dependence of the tensile strength is given by the equation of Williams, Landel, and Ferry[8] which is applicable in the temperature range $T_g < T < (T_g + 100)$. Bueche reported some tensile data for polybutyl methacrylate which has a glass transition temperature of 8° C. These tensile data were measured under various constant loads at temperatures between 30 and 95° C, and reasonable agreement between theory and experiment was found. Although Bueche did not consider the ultimate elongation, it seems reasonable that such data can be superposed by using the same shift factor as required to superpose the tensile strength data.

Other workers have not considered explicitly the effect of viscous forces on the ultimate properties but have considered the effect of such variables as molecular weight, degree of crosslinking, and plasticizers[1,9–11].

The present investigation was made to determine the effect of a wide variation in temperature and strain rate on the tensile strength and ultimate elonga-

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tion of a crosslinked elastomer. A SBR rubber polymerized at 50° C was chosen for study since this material has not been known to crystallize under any ordinary conditions of temperature or elongation[12,13]. Although some stress relaxation data reported by Mooney and Wolstenholme[14] indicate that SBR may crystallize or at least form small ordered aggregates when deformed for long periods, no evidence exists which indicates that crystallization occurs under the more usual experimental conditions.

The present study had the following specific objectives: (1) to determine whether or not composite curves could be obtained which show the variation of tensile strength and ultimate elongation with reduced strain rate, (2) to determine if the temperature dependence of the ultimate properties is given by the Williams, Landel, and Ferry equation, and (3) to compare the strain rate dependence of the tensile strength with Bueche's theory.

EXPERIMENTAL

The SBR gum vulcanizate was supplied by Mr. F. L. Roth of the National Bureau of Standards. The SBR had been prepared by emulsion polymerization at 50° C for a reference standard and contained about 23.5% bound styrene. (The exact amount was not measured.) The gum vulcanizate contained the following parts by weight: SBR 1000, 100 parts; zinc oxide, 5 parts; sulfur, 2 parts; and mercaptobenzothiazole, 1 part. The sheets were cured for 45 minutes at 150° C. Two rough determinations of the glass transition temperature—made using a dilatometer with isooctane as the confining liquid—gave an average value of −63°, which is in good agreement with −61° reported for a SBR containing 25.5% bound styrene[15].

The tensile specimens used were rings cut from the sheets of SBR with a special cutter mounted in a drill press. These rings had a rectangular cross section, as near as could be determined by visual observation. The dimensions of a number of rings were measured, and average values of the inside diameter (i.d.), outside diameter (o.d.), thickness, and width were used in the calculation of tensile data. The average dimensions in inches were as follows: o.d., 1.522; i.d., 1.342; thickness, 0.081; and width, 0.090. All rings were weighed, and those whose weight deviated from the average by more than about 4% were discarded. The variation in weight showed that the rings were not identical in size. And it was found that some of the scatter in the experimental values for tensile strength and ultimate elongation could often be correlated with the variation in weight.

Tensile data were measured with an Instron tensile tester at fourteen temperatures between −67.8 and 93.3° C and at as many as eleven strain rates between 0.158×10^{-3} and 0.158 sec^{-1}. (Measurements were made at the lowest strain rate at only eight temperatures: −34.4, −12.2, 25, 43.3, 60, 71, 87.8, and 93.3° C.) The Instron tester was equipped with a telescoping air thermostat which contained armholes for changing tensile specimens and a small window for viewing specimens during a test. A blower activated by a bimetallic thermoregulator circulated air through the thermostat from a large Aminco temperature conditioning cabinet which was either cooled with dry ice or heated with electric heaters. The temperature in the vicinity of a tensile specimen did not vary by more than ±1° F during any test, although the temperature in different parts of the thermostat sometimes differed by 2 to 3° F, as measured by three thermocouples.

The rings were conditioned in the thermostat for about one hour and then

tested by placing over hooks (similar to those described by Clifford and Gehman[16]) attached to the crosshead and load cell of the Instron. A thin film of silicon grease was used on the hooks to facilitate slippage of a ring during test.

During a test, the Instron recorder gives a curve of pounds force against time. The force was converted into nominal stress by dividing by twice the cross sectional area of a ring. Since the crosshead travels at constant speed, the time axis is proportional to the crosshead displacement. Thus, the strain γ was calculated from the crosshead displacement ΔC using the equation

$$\gamma = \frac{2\Delta C}{\pi(\text{i.d.})} \tag{1}$$

where i.d. is the inside diameter of the rings. The inside diameter was used instead of the average ring diameter, which is often used[16,17]. This was done since as a ring is elongated the outside is stretched less than the inside, and thus the elongation on the inside determines when a ring will rupture. In a separate study made using rings with various diameters and with o.d/i.d. ratios between 1.1 and 1.8, it was found that the ultimate elongation was essentially independent of o.d/i.d. only if the elongation was calculated using the i.d. When the average diameter was used, the elongation decreased by about 30% as o.d./i.d. ratio increased from 1.1 to 1.8. From this study, it was concluded that the most reliable values of ultimate strain are obtained (1) by calculating strain using the inside diameter, and (2) by using rings whose o.d./i.d. ratio is 1.1 or less.

An indication of the reliability of the tensile data obtained using SBR rings was found by testing five dumbbell-shaped tensile specimens at a crosshead speed of 2.0 in./min at 25° C. The dumbbell specimens had a 2.0-in. gage section and an effective gage length of 3.2 in.[18] The average value of the tensile strength for the dumbbell specimens was 227 lb/in.^{2} which compares favorably with 242 lb/in.^{2} shown in Figure 1 and 204 lb/in.^{2} obtained from the composite plot in Figure 4. The average ultimate strain for the dumbbell specimens was 3.55 which is in acceptable agreement with 3.7 and 3.3 obtained from the curves in Figures 2 and 5, respectively.

The average molecular weight between crosslinks M_c for the SBR was determined from both equilibrium swelling data and the equilibrium rubbery modulus. Duplicate swelling measurements were made at 25° C in carbon tetrachloride, *p*-xylene, toluene, and benzene. Laboratory reagents were used without purification. Small, weighed pieces of SBR were placed in the solvents, removed periodically, and weighed in stoppered weighing bottles after removing excess solvent with filter paper. The measurements were continued for 31 days, although no detectable change in weight occurred after about two days. Satisfactory agreement between duplicate determinations was obtained.

Values of M_c were calculated using the equation[9]

$$-[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] = \frac{\rho V_1}{M_c}\left(v_{2m}^{\frac{1}{3}} - \frac{v_{2m}}{2}\right) \tag{2}$$

where v_{2m} is the volume fraction of SBR at equilibrium, ρ the density of SBR, M_c the average molecular weight between crosslinks, V_1 the molar volume of solvent, and χ_1 the solvent-polymer interaction parameter. It was assumed

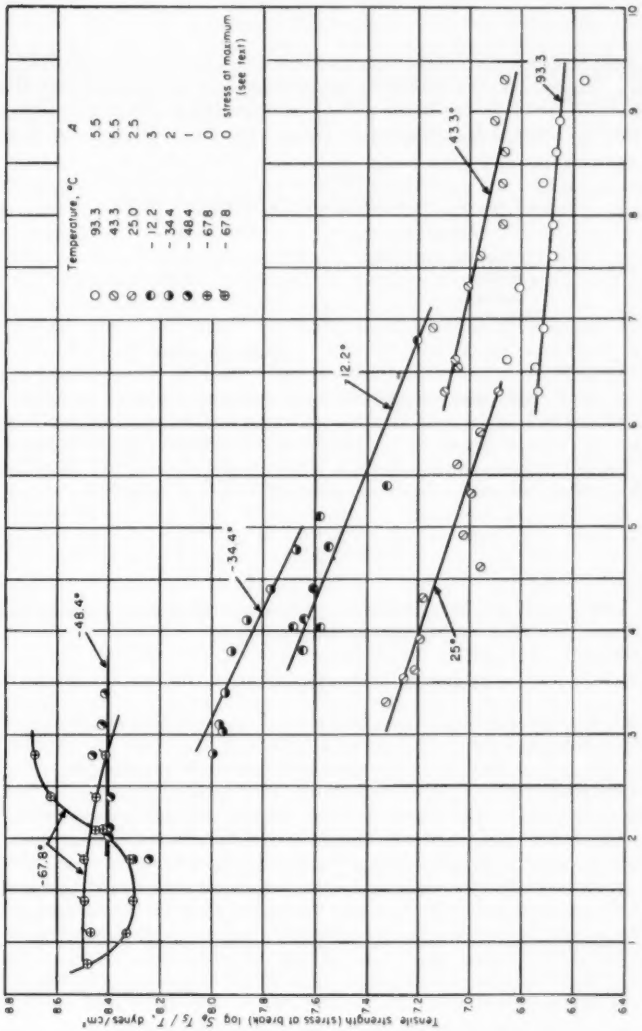

FIG. 1.—The variation of tensile strength with strain rate R at seven temperatures between −67.8 and 93.3° C.

that χ_1 is given by the equation[19]

$$\chi_1 = 0.3 + \frac{V_1(\delta_1 - \delta_2)^2}{RT} \tag{3}$$

where δ_1 and δ_2 are the solubility parameters for the solvent and SBR, respectively. Values for the solubility parameter δ_1 were taken from Hildebrand and Scott[20], and δ_2 was taken as 8.60, as reported by Scott and Magat[19]. The calculated values of M_c are listed in Table I and the average value is 8020.

TABLE I

VALUES OF M_c FROM EQUILIBRIUM SWELLING DATA

Solvent	M_c
Carbon tetrachloride	8000
p-Xylene	8657
Toluene	8000
Benzene	7424
Average	8020

A value of M_c was also calculated from stress-strain data measured at 87.8° C. These data measured at different rates are shown in Figure 7 on a log-log plot of reduced stress vs. reduced strain[18] with the stress reduced to 263° K. From this plot, the equilibrium Young's modulus at 263° K is found to be 6.95×10^6 dynes/cm^2. Upon substituting in the equation[9]

$$M_c = \frac{3\rho RT}{E} \tag{4}$$

using $\rho = 0.98$ g/cm^3, a value of 9250 is obtained for M_c which is in reasonable agreement with 8020 obtained from the swelling data.

RESULTS AND DISCUSSION

The rate dependence of the tensile strength S_b and ultimate strain γ_b at seven temperatures are shown in Figures 1 and 2. Figure 1 shows plots of log S_bT_s/T vs. log $1/R$, where T_s is the standard reference temperature 263° K (discussed subsequently), T the temperature of measurement in ° K, and R the strain rate in sec^{-1}. (Abscissa values are shifted arbitrary amounts A for clarity.) The tensile strengths are multiplied by the factor T_s/T, since the elastic retractive forces in polymeric chains are proportional to the absolute temperature according to the statistical theory of rubberlike elasticity and this factor should be included before tensile strengths at different temperatures are compared. It is seen that S_b increases with increasing strain rate and decreasing temperature except at −67.8° where cold-drawing occurred. Cold-drawing also occurred at −53.8° and at −48.4° at strain rates greater than 0.04 sec^{-1} (5 in./min crosshead speed). The values of S_b under such conditions appeared erratic and tended to decrease with increasing rate.

When cold-drawing occurred, the nominal stress-strain curves passed through a maximum at small strains, ca. 0.1, and then the stress either remained relatively constant or varied erratically until all of the material was cold-drawn. The stress at the maximum was found to increase only slightly with strain rate at −67.8°, as shown in Figure 1. However, at −53.8°, the

stress at the maximum increased from 5.78×10^7 to 1.65×10^8 dynes/cm^2 as the strain rate increased from 0.158×10^{-2} to 0.158 sec^{-1}. The strain at the maximum was found to be about 0.1 and was independent of strain rate and temperature within the experimental accuracy. However, the ultimate strain varied greatly with the strain rate. From a study of the cold-drawing of oriented polystyrene monofilaments, Andrews and McMurray[21] report observations in agreement with the above, except that they report that the ultimate strain is independent of rate.

The cold-drawing of a SBR ring was carefully observed at $-67.8°$. When subjected to a small elongation, the ring turned lighter in color at one or two spots, and then a neck or shoulder formed at these spots. The thickness of the constricted portion was estimated to be about half that of the undrawn portion. Upon continued stretching, the neck progressed slowly around the ring while the stress remained relatively constant. After all of the ring was cold-drawn, the specimen either broke or underwent further elongation with an increase in stress, depending on the temperature and strain rate.

Marshall and Thompson[22] attributed cold-drawing to a temperature rise produced by stretching a specimen. After a neck forms, heat flows from the neck to the undrawn portion. Hence, the data obtained for SBR at the two or three lowest temperatures may not represent the isothermal properties of the material at these temperatures, and perhaps the data should not be included in composite plots, discussed subsequently.

In Figure 2, the dependence of the ultimate strain on strain rate is shown. At temperatures above $-34.4°$, the strain increases with increasing strain rate and decreasing temperature. Below $-34.4°$, the strain decreases with increasing strain rate, while at $-34.4°$ the strain passes through a maximum at a strain rate of about 0.02 sec^{-1}. Data obtained at seven additional temperatures lie among the lines shown in Figures 1 and 2. Although straight lines have been drawn through most of the data shown, the points probably would define curves which are segments of a master curve if data of sufficient accuracy were available. All of the points shown in Figures 1, 2, 4, and 5 are from single measurements except at 25 and 87.8° C where averages of duplicate tests were used. At some temperatures, two points are shown at one or more strain rates which indicates that duplicate tests were made.

The data in Figures 1 and 2 suggest that both the tensile strength and ultimate strain at the different temperatures can be combined to yield composite plots. As mentioned previously, Bueche's[7] theory predicts that tensile data can be superposed by using the same shift factor a_T which is used to superpose viscoelastic data measured in small deformations. (The quantity a_T equals approximately the ratio of the frictional coefficient for polymer segment mobility at temperature T divided by its value at some reference temperature. For a discussion of a_T and its temperature dependence, see ref. 8.)

Three independent methods were used to obtain experimental values of $\log a_T$ for SBR: (1) the tensile strength data were shifted along the $\log 1/R$ axis until the curves at different temperatures superposed; (2) the ultimate strain data were shifted in a similar manner; and (3) stress-strain curves measured at different strain rates and temperatures were superposed as described elsewhere[18]. At a single temperature, stress-strain curves measured at different strain rates superpose on a plot of $\log \alpha S T_0/RT$ vs. $\log \gamma/R$, where α is the principal extension ratio and T_0 is some reference temperature, provided the material exhibits linear viscoelastic behavior. Stress-strain curves for SBR measured at different rates were found to superpose with excellent pre-

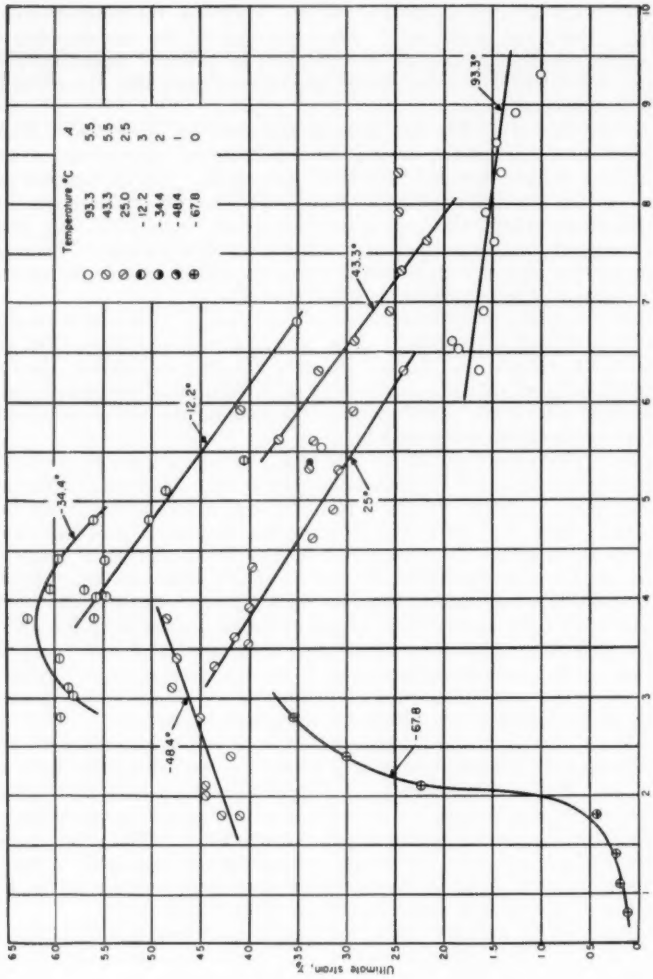

FIG. 2.—The variation of ultimate strain with strain rate R at seven temperatures between −67.8 and 93.3° C.

cision, often for elongations up to 200% or more. To determine log a_T, plots of log $\alpha ST_0/RT$ vs. log γ/R at different temperatures are shifted along a line of unit slope until they coincide; the distance shifted equals log a_T.

Values of log a_T obtained by the three independent methods are shown in Figure 3. Log a_T could not be obtained from stress-strain curves above 25° C since the plots of log $\alpha ST_0/RT$ vs. log γ/R has a slope near unity which precluded an accurate evaluation of log a_T by shifting to give superposition.

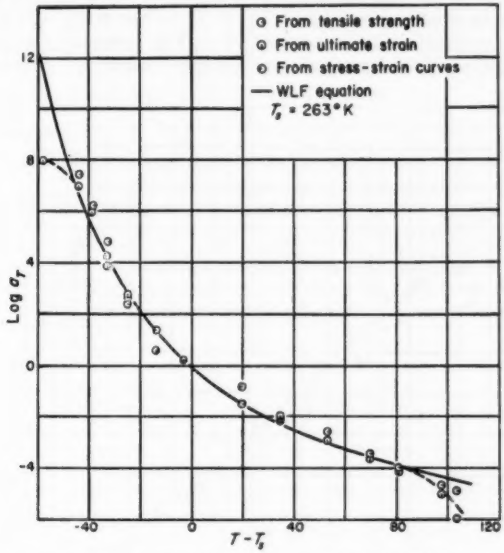

FIG. 3.—Experimental values of log a_T compared with the WLF equation.

The temperature dependence of log a_T is given in the range $T_g < T < (T_g + 100)$ by the Williams, Landel, and Ferry[8] (WLF) equation

$$\log a_T = \frac{-8.86(T - T_s)}{101.6 + T - T_s} \tag{5}$$

where T_s is a standard reference temperature which has been found to be about 50 ± 5° above T_g for a wide variety of polymers, organic glass-forming liquids, and inorganic glasses. By comparing a plot of log a_T vs. T for SBR with Equation (5) plotted as log a_T vs. $(T - T_s)$, T_s was found to be 263° K. Thus, if T_g is 50° below T_s, the experimental values of a_T give −60° for T_g which is in good agreement with −63° obtained dilatometrically.

The solid line in Figure 3 was calculated from Equation (5) with T_s = 263° K. It is seen that the WLF equation fits the experimental values of log a_T between −53.8° and 71° C, within experimental error. At −67.8° the value of log a_T lies below the theoretical curve, which is not surprising since cold-drawing occurred during the tensile tests; also, −67.8° is below T_g where the WLF equation is not applicable. Since the WLF equation is usually believed

to hold only in the range $T_g < T < (T_g + 100)$, the log a_T values at the higher temperatures might be expected to be below the solid line, as has been observed for other polymers[8]. However, it appears from the sharp drop in experimental a_T values at 87.8 and 93.3° that some thermal degradation of the SBR may have occurred at these high temperatures. But it can be concluded that over a temperature range of more than 120° the temperature dependence of the ultimate properties is given within experimental error by the WLF equation.

To construct composite curves, values of log a_T were used as given by the WLF equation in the range $-53.8 < {}^\circ C < 71$ and as given by the dotted line in Figure 3 at −67.8°, 87.8°, and 93.3° C. The resulting composite curves reduced to −10° C (263° K) are shown in Figures 4 and 5. It is seen that the

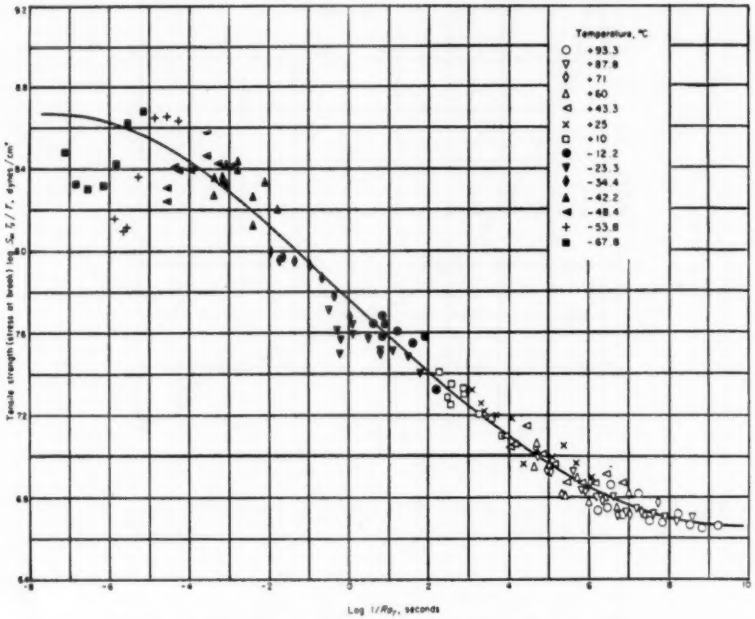

FIG. 4.—The variation of tensile strength with reduced strain rate Ra_T.

tensile strength increases monotonically with increasing strain rate, except when cold-drawing occurred, but that the ultimate strain increases from about 125 to 600% and then drops rapidly to zero.

Since ultimate property data are not too reproducible—a slight flaw or variation in cross sectional area can greatly affect the break point—the scatter of points about the curves is not unduly great. Actually, the majority of strain values lie within 10% of the curve, and few deviate by more than 20%. Also, essentially all of the tensile strengths lie within 0.1 logarithmic unit from the curve, except values at the lowest two or three temperatures where cold-drawing occurred.

From the two composite curves and values of log a_T, the tensile strength

and ultimate strain can be predicted at any temperature and strain rate, provided under test conditions heating effects and effects due to the propagation of stress waves are negligible. At very high strain rates the stress may not be uniform throughout a test specimen, due to the finite velocity for the propagation of a stress wave. And so values for the ultimate properties measured under impact types of loading may differ from values predicted from the composite curves. Although the heat build-up in a tensile specimen during a test has not been considered in detail, it will be most pronounced at low temperatures and at high rates. Thus, the predicted properties at high strain rates should be most reliable at high temperatures where heating effects will be the smallest. But predicted properties at very low strain rates should be reasonably reliable over the entire temperature range.

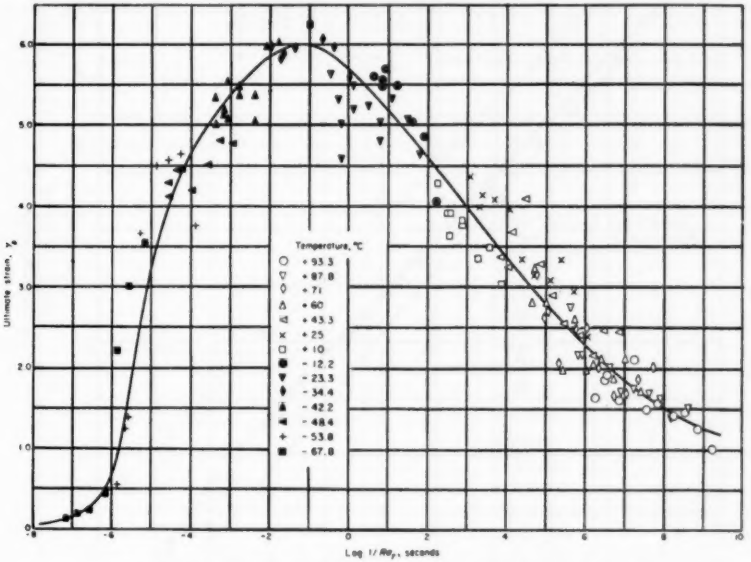

FIG. 5.—The variation of ultimate strain with reduced strain rate Ra_T.

Figure 6 shows the reduced stress-strain curve, i.e., a plot of $\log \alpha S T_0/TRa_T$ vs. $\log \gamma/Ra_T$, obtained by combining stress-strain curves measured between -48.4 and $25°$ at strain rates between 0.158×10^{-3} and 0.158 sec^{-1}. Data on elongations greater than 300% are not shown, although at nearly all of the temperatures and strain rates at least one point obtained at elongations greater than 200% is shown. Data obtained at temperatures below $-48.4°$ are not included owing to the cold-drawing that occurred at elongations greater than 10%. Points from stress-strain curves measured above $25°$ are not shown, although they all fall on the line of near-unit slope which is shown.

The dotted line in Figure 6 represents the ultimate properties of SBR. It was constructed using data obtained from the smooth curves shown in Figures 4 and 5. It should be noted that the dotted line approaches the solid line at both large and small values of the reduced strain γ/Ra_T. But at intermediate

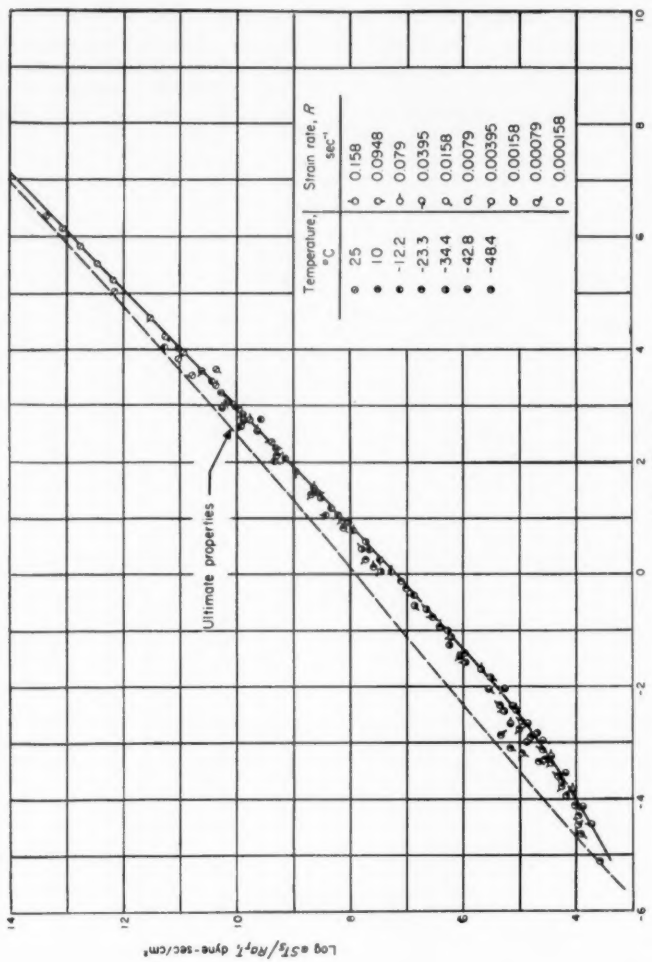

FIG. 6.—Stress-strain curves reduced to unit strain rate and 263° K compared with ultimate properties (- -) reduced to the same temperature.

values of the reduced strain, the dotted line lies considerably above the reduced stress-strain curve. A stress-strain curve measured at some given strain rate and temperature follows the reduced stress-strain curve for elongations up to about 200% and then breaks upward from the reduced curve. When the stress-strain curve intersects the dotted line, the sample will break.

Stress-strain curves measured at different strain rates at 87.8° are shown in Figure 7 on a plot of $\log \alpha S T_s/R(361)$ vs. $\log \gamma/R$, where T_s is 263° K. The circles are values calculated from the individual stress-strain curves, and the squares are the values at which rupture occurred. It is seen that the super-

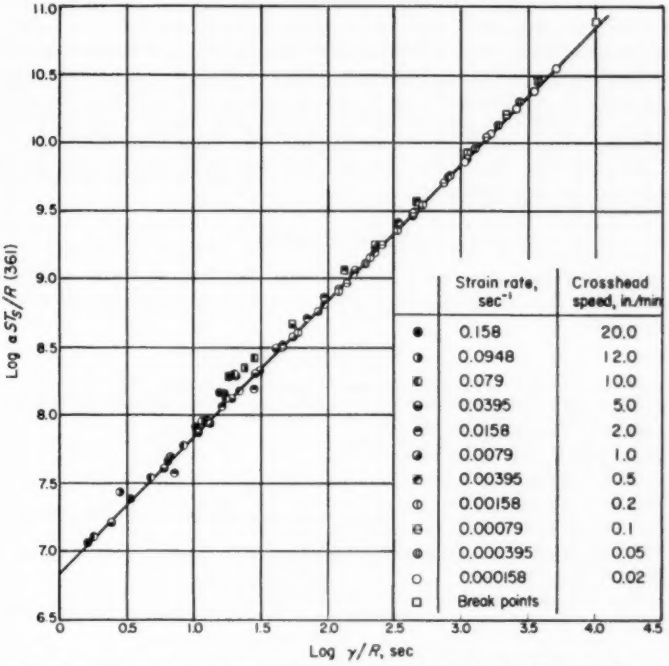

FIG. 7.—Stress-strain curves measured at different strain rates and 87.8° C reduced to unit strain rate; stress reduced to 163° K.

position is good and that the break points lie only slightly above the solid line. The solid line was drawn with unit slope which indicates that viscous forces are essentially zero. Thus, the line is the equilibrium stress-strain curve at 263° K.

The theoretical curve calculated by Bueche[7] for the variation of tensile strength with strain rate will superpose with the experimental data shown in Figure 4 only for values of $\log 1/Ra_T$ greater than about 7.0. At smaller values of $1/Ra_T$, the theoretical curve increases much more rapidly than the experimental one. In calculating the theoretical curve, a correction involving Young's modulus, which becomes important only at high strain-rates, was omitted. It is believed that the inclusion of this correction in the calculation

would not modify sufficiently the shape of the theoretical curve so that it would fit the experimental data over the extended time-scale shown in Figure 4.

SYNOPSIS

The tensile properties of an unfilled SBR rubber were measured with an Instron tensile tester at strain rates between 0.158×10^{-3} and 0.158 sec^{-1} and at fourteen temperatures between -67.8 and 93.3° C. The tensile strength and ultimate strain at the various strain rates and temperatures were superposed to give two composite curves which are functions of a reduced strain rate. From this superposition, the temperature dependence of the ultimate properties was obtained. The temperature dependence between -53.8 and 71° is essentially the same as obtained by superposing the stress-strain curves and is given by the Williams, Landel, and Ferry equation. From the composite curves and the temperature function, the tensile strength and the ultimate strain can be predicted at any strain rate and temperature, provided heating and wave propagation effects are negligible. The linear viscoelastic properties were obtained from the initial portions of stress-strain curves and are represented by a reduced stress-strain curve.

ACKNOWLEDGMENT

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THERMAL EXPANSION MEASUREMENTS AND TRANSITION TEMPERATURES, FIRST AND SECOND ORDER *

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INTRODUCTION

When any pure material goes through a change in state, its physical properties change greatly. In each phase the physical properties are relatively constant or change slowly enough with temperature that the rate of change of a property such as volume is a constant. This rate of change of volume is the thermal expansion coefficient, $(\partial V/V)/\partial T$.

The thermal expansion coefficient is almost constant, experimentally, as long as the temperature range over which measurements are made does not include a phase transition. At the transition temperature, abrupt changes in volume are found as illustrated in Figure 1.

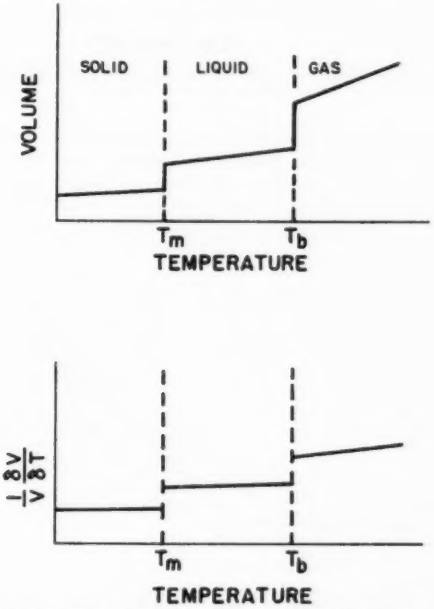

FIG. 1.—Typical changes in volume and coefficient of expansion for ordinary materials.

* Reprinted from the *Journal of Applied Polymer Science*, Vol. 1, Issue 1, pages 121–126 (1959). Presented in part to the High Polymer Division of the American Physical Society, Chicago, March 29, 1958.

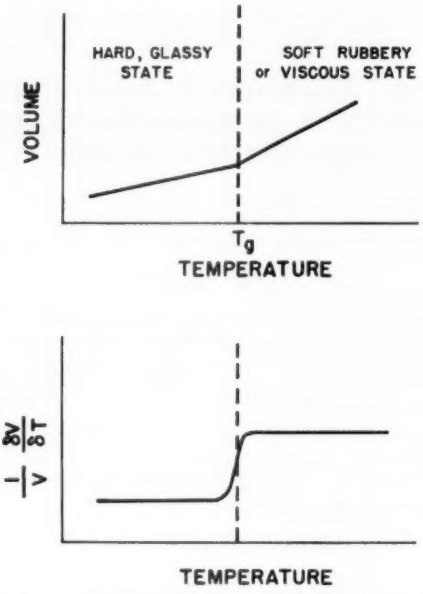

FIG. 2.—Typical changes in volume and coefficient of expansion for amorphous polymeric materials.

Polymeric materials often show changes in physical properties not necessarily accompanied by abrupt changes in volume, even though the expansion coefficient does change. Since the expansion coefficient changes, some change in internal structure is suspected, and the name second-order transition (T_g) has been adopted. This kind of change is roughly diagrammed in Figure 2.

This latter change at the second-order transition temperature can be found in every known polymer, even though many polymers possess clear, first-order,

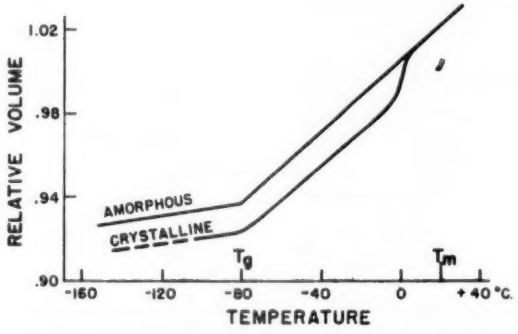

FIG. 3.—Changes in volume of Hevea rubber showing both crystalline and amorphous transitions.

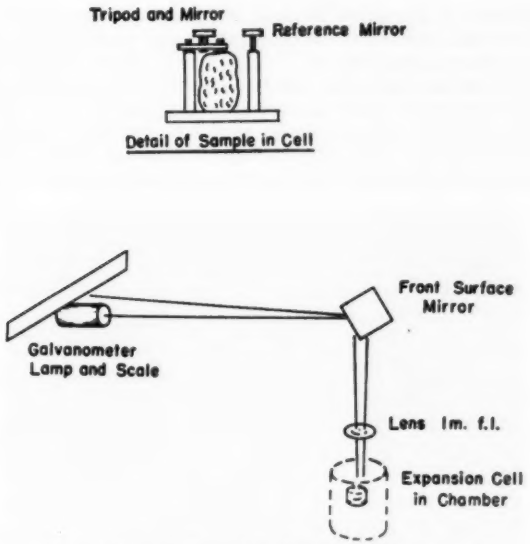

FIG. 4.—Schematic illustrations of experimental arrangements.

crystalline transitions as well. Hevea rubber, for example, has a crystalline melting point of 28° C, compared to its T_g about −70°. These data are shown, copied from Boyer and Spencer[1], as Figure 3.

APPARATUS

Since the transition which takes place at any observed temperature is accompanied by changes in the other physical properties, an attempt was made to identify transitions in some new polymers to aid in the understanding of their

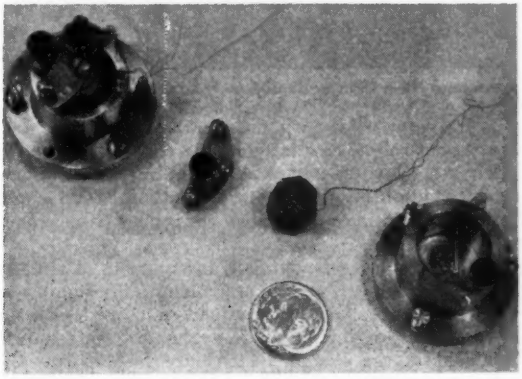

FIG. 5.—The loaded differential expansion cell and components.

other properties. A simplified form of dilatometer utilizing the principle of differential thermal expansion was constructed and modified in two important ways from a design published by K. L. Floyd[2]. Since some polymers were very difficult to prepare and only limited amounts were available, sample size was reduced to about one cubic centimeter. Also, direct and continuous measurement of temperature eliminated the need for a constant temperature bath, and further removed the restrictions imposed by contact fluids. An additional advantage accrued in that the thermal range of measurement was increased.

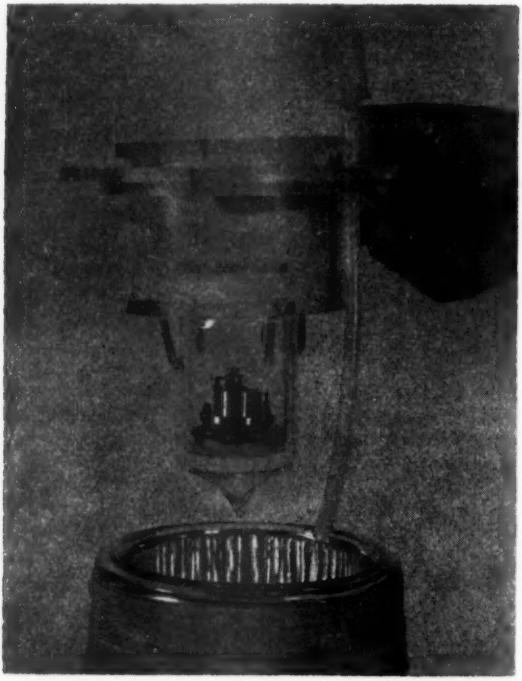

FIG. 6.—The expansion cell in vacuum wall flask ready for a cooling cycle run. Liquid nitrogen can be poured into the Dewar flask through the polyethylene sidearm.

The apparatus, basically, is a dilatometer in which the actual dilation of the sample is measured mechanically in one chosen direction or dimension; that is, this is a linear differential thermal expansion method. The length of a sample is compared to that of a stainless steel post, conveniently hollowed to form a cup which holds the sample.

The apparatus is sketched schematically in Figure 4. Details of the cup and tripod are shown in Figure 5. Several assemblies, differing in size and in kind of metal, have been made. The mirror tripod rests one leg on the sample, the other two on the stainless steel cup. A washer prevents indentation of the sample. Movement of the sample relative to the cup tips the tripod and mirror, and thus moves the galvanometer spot. An auxillary mirror on the

cup checks zero, making the differential measurements independent of slight shifts in the level of the cup. The sample may range from 10 to 12 mm in height, but must have fairly flat faces. Clean, knife-cut surfaces are acceptable. The sample need not be cured, since creep can usually be reduced to a negligible value by appropriate heat or relaxation treatments.

Temperature of the sample is measured by an iron-constantan thermocouple inserted close to the midpoint. The thermocouple is made of No. 38-gage wire to eliminate false movements of the sample arising from the springness of

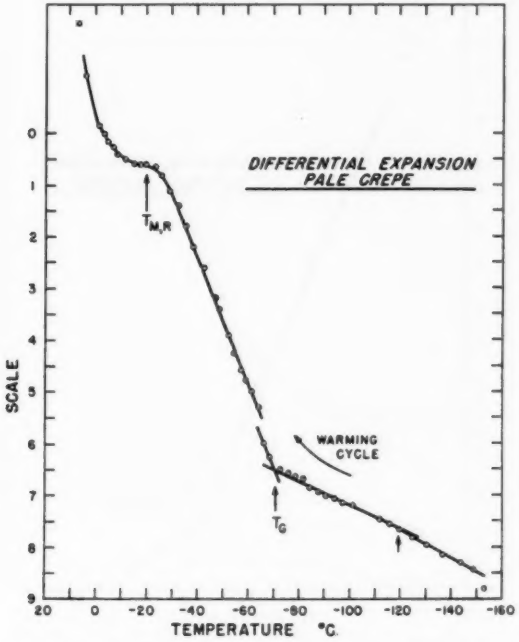

FIG. 7.—A typical differential expansion curve for a sample of pale crepe.

heavier gage wires. An ice junction is used. Individual calibrations of the junctions are not attempted, since values read from tables are considered accurate enough.

Two alternate procedures have been used, the first being preferred as more convenient. In the first procedure, the assembled cup containing the sample and tripod is flooded with liquid nitrogen in an insulated chamber or in a vacuum flask. After the excess nitrogen has boiled away, expansion of the samples in warming to room temperature is followed. The rate of rise near $-150°$ C is about 1° per minute; near 0°, less than ½° C per minute. With this initial, fairly rapid, temperature rise, the sample is not at constant temperature throughout. The gradient is estimated at 3° C maximum, but may be less. In the second procedure, the assembled cup is placed in a vacuum wall flask, which, in turn, is immersed in liquid nitrogen. In this procedure, the sample

cools slowly by radiation to the cold surroundings. Similar measurements of contraction with decreasing temperature can be followed. Multiple windows enclosing dry, dead air spaces permit observations without excessive frosting troubles. The expansion cell in its chamber is shown in Figure 6. The data are usually plotted as galvanometer curves vs. temperature. Breaks or discontinuities identify transitions. Coefficients of expansion were computed from smoothed curves in some cases.

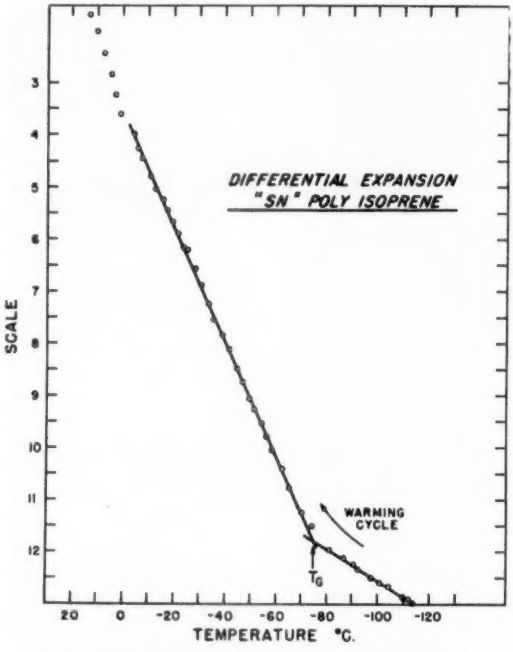

FIG. 8.—A typical differential expansion curve for a sample of SN rubber (polyisoprene, about 95% *cis* 1,4-structure).

POLYMER TRANSITIONS

A typical expansion curve for a sample of pale crepe natural rubber is shown in Figure 7. Quick cooling with liquid air is followed by linear expansion as the cell and sample warm up. At about $-70°$ C the sample increases its rate of expansion, clearly defining the second-order transition temperature. The break at about $-60°$ C is due to relaxation of stress frozen in by the shock cooling of direct contact with the liquid air. This break, in contrast to other changes, is irregular, not repeatable, and can be eliminated by slower cooling techniques. Further increase in temperature is accompanied by linear expansion up to about $-25°$ C, at which temperature the rubber crystallizes rapidly. The decreased height and increased rate of rise of temperature are related to the increased density of the crystalline phase and the liberation of the latent

heat of crystallization. Further warming results in a more rapid expansion as the crystalline phase melts to the amorphous rubber. The small change in slope to about −125° C is believed to be an artifact of the stainless steel used in the cell, in that this material undergoes a first-order phase change at about this temperature. A pure nickel cell has been used to check ambiguities of this kind.

A similar expansion curve for a sample of Ameripol SN is shown in Figure 8. This material is polyisoprene, polymerized about 95% as the *cis*-1,4-isomer. Rapid cooling followed by slow warming shows the same change in expansion but at about −75° C. Further warming shows no evidence of crystallization.

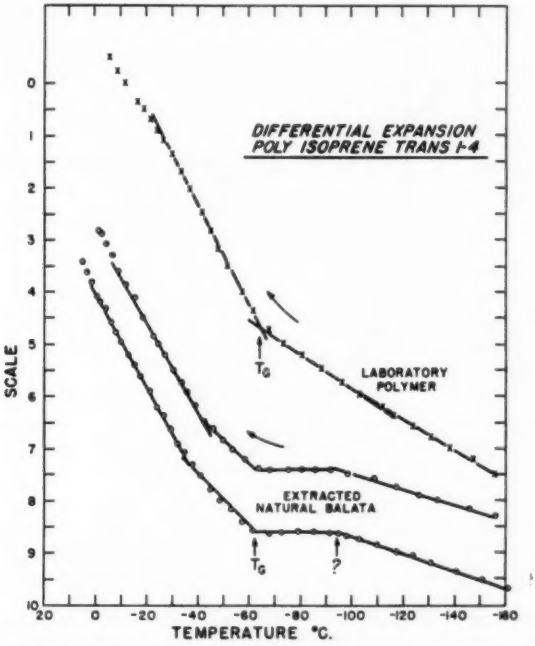

FIG. 9.—Typical differential expansion curves for polyisoprene, *trans*-1,4-structure.

This lack of crystallinity merely reflects the purity of the material, in that nucleating centers for the crystalline phase are not present in sufficient concentrations to initiate this action in the time duration of this run. Other independent measurements have shown crystallization rates and crystal phase structure identical with natural rubber when the proper seeding impurities are added. The same transition temperature, −75° C, was obtained for a highly purified sample of natural rubber furnished by Dr. D. Craig of this laboratory.

Expansion curves for samples of extracted balata and a laboratory-polymerized polyisoprene are shown in Figure 9. The experimental polymer was believed to have a *trans*-1,4-isomer content over 90% and was a hard, leathery material at room temperature. The abrupt change in expansion about −60° C

is clear evidence for the glass transition, even in the presence of the crystalline phase. The two curves for the natural balata were obtained on specimens cut from the same original sheet about a week apart. Both curves show the same breaks and changes, confirming each other very nicely. The glass transition at $-60°$ C is clearly identifiable. The change in slope at about $-80°$ C cannot be explained.

Expansion curves for several samples of polybutadiene with *cis*-1,4-isomer contents of about 95% have been obtained, all of which can be made to show certain common features illustrated in Figure 10. Shock cooling followed by warming causes expansion in the glassy state. The increase in the rate of

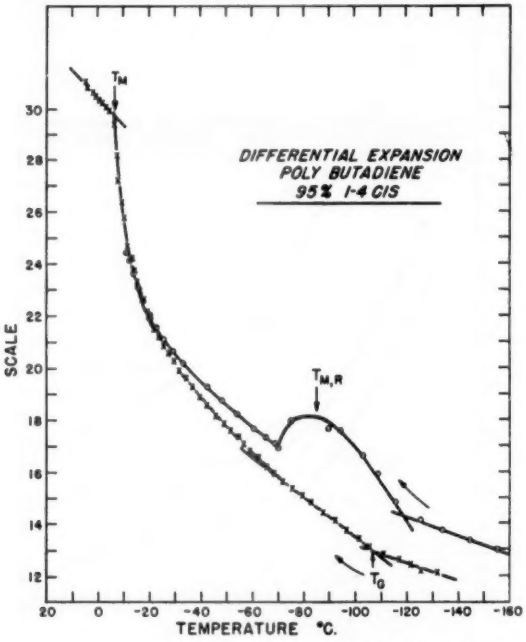

FIG. 10.—Typical differential expansion curves for polybutadiene, 1,4-structure.

expansion above about $-120°$ for the data shown is accompanied by an abrupt increase in the rate of warming to about 15° C per minute, in contrast to the $\frac{1}{2}$° C per minute at both lower and higher temperatures. This peculiar volume change obviously is evidence of rapid crystallization at about $-85°$ C, apparently starting at much lower temperatures. Curves of this type are not uniformly reproducible either in the "crystallization hump" or in the value of T_g. Reproducible curves can be obtained by slower cooling, followed by warming of the type also shown in Figure 10. Expansion changes abruptly at about $-108°$ C, then continues linearly up to about $-70°$ C. Deviations from linearity above this temperature are believed to represent partial melting of the crystalline phase of this material. Melting in this specimen is complete at

$-6°$ C. While the T_g is not sensitive to changes in structure in the range above about 85% isomer content, the final melting temperature T_m decreases as the *cis* content falls from 100%. The melting point of the 100%-*cis* polymer cannot be estimated from these data, since the influence and amount of impurities are too difficult to measure or estimate with confidence.

Expansion curves for two samples of polyethylene and a sample of polymethylene are shown in Figure 11. The high-pressure polyethylene, after shock cooling, shows a linear expansion with a distinct change in slope at about $-125°$ C. The subsequent expansion curve has no extensive linear region,

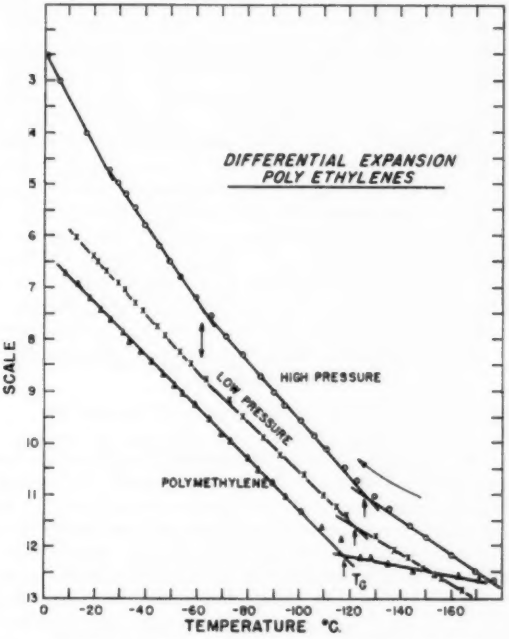

FIG. 11.—Typical differential expansion curves for polyethylenes.

although it has been drawn or approximated by a series of chords. The low pressure polyethylene similarly shows a distinct break at about $-122°$ C, followed by linear expansion over a considerable temperature range. Subsequent expansion does not follow the same linearity, but the question about continuous curvature cannot be resolved. The sample of polymethylene, furnished by Dr. Franz Widmer, shows linear expansion up to $-120°$ C, followed by further linear expansion at a different slope. The change in behavior of these three materials is believed to be significant and related to differences in their structure.

Expansion curves for samples of polypropylene and poly-1-pentene are shown in Figure 12. Both materials are isotactic polymers showing crystallinity at and above room temperature, with melting points near 150° and 75° C,

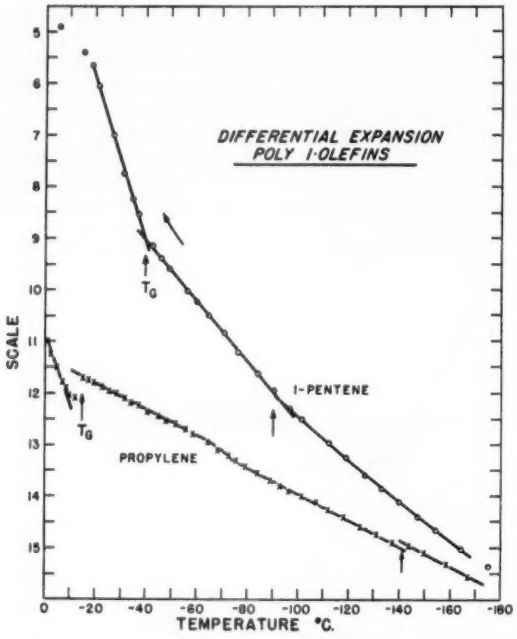

FIG. 12.—Typical differential expansion curves for polyolefins.

respectively. Both warming and cooling curves show the second-order transitions for polypropylene at about −20 and about −40° C for poly-1-pentene. Additional repeatable changes in the expansion curves can be identified, although their significance cannot be explained. It can be noted that the expansion curves for these two polymers differ in slope just below T_g, but are fairly comparable above that temperature. The coefficient of expansion below T_g has been computed from the graph and instrument constants and it is presented in Table I, together with similar information on other comparable polymers. The values of $\partial l/\partial T$ are reliable only to about 10%, since the tipping arm of the optical lever is difficult to measure accurately. Also listed are the

TABLE I

TRANSITION TEMPERATURE AND EXPANSION COEFFICIENT

Polymer	T_g, °C	$1/l\left(\frac{\partial l}{\partial T}\right)_{T<T_g}$ ×10⁵ cm/cm °C	T_f, °C
Polyethylene (high pressure)	−125	8	
Polyethylene (low pressure)	−122	7	
Polypropylene	− 20	6	− 70
Poly-1-butene	− 25	12	− 80
Poly-1-pentene	− 40	15	− 90
Poly-1-hexene	− 50	16	−110
Poly-1-octene	− 65	23	−105

temperatures of the additional low temperature discontinuity in the column labeled T_γ. The small change in slope makes these values less reliable than the corresponding T_g measurements.

DISCUSSION

Differential expansion measurements on a variety of polymers have shown changes in state easily recognizable as first-order crystalline and/or second-order glassy phenomena. In addition to these obvious transitions, some materials show reproducible discontinuities in slope which can be interpreted as additional second-order transitions. If these discontinuities represent a loss of a degree of freedom for some portion of the molecule, then changes in dynamic mechanical properties would be expected in the vicinity of these temperatures. Changes of this kind have been reported before [3,4] and where comparisons can be made, seem reasonable in magnitude.

The change in the expansion coefficient just below T_g, where the polymers are presumably in corresponding states, indicates that the polyolefins with the larger side groups retain excess volume as they cool from above the glass transition. The retention in volume is roughly proportional to the number of carbon atoms in the side chain. An alternate interpretation states that each side chain methylene group adds a constant increment of nonoccupied volume to the molar volume of the backbone chain. The expansion value for the polyethylenes is higher than for polymethylene, and is also out of place in the polyolefin series. This may be taken as further evidence of the side group structure of these materials, but any estimation of amounts or kinds of side structure are not justified.

SYNOPSIS

Transitions in polymers have been studied with the use of a differential expansion apparatus modified from a design described by K. L. Floyd. Materials ranging from uncured, soft rubbers to hard, waxy solids have been studied from above room temperature down to liquid air temperatures. Both the first-order transition temperature, T_m, and the second-order transition temperature, T_g, can be identified. Multiple changes in slope of the expansion curves indicate the possibility of additional second-order transitions. Expansion curves for several diene rubbers are presented, illustrating typical transition phenomena. Expansion curves for several polyolefin materials are presented which illustrate changes in T_g and in the low temperature expansion coefficient with changes in the structure of the polymer.

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THERMOELASTIC PHENOMENA IN SKS-30A AND SKB RUBBER COMPOUNDS IN ADIABATIC DEFORMATION *

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The thermal properties of substances such as rubber change substantially on deformation. Stretching (to 300–350%) and relaxation of noncrystallizing rubbers is accompanied by the evolution and absorption of heat corresponding to the work of deformation. This directly indicates the kinetic character of the elastic forces[1].

The nature of the elastic forces and the condition of the material at high elongations (before break) can be determined by studying the laws of conversion of work into heat during adiabatic deformation.

We have studied the thermoelastic phenomena occurring during deformation up to breaking in gum and filled SKS-30A and SKB rubbers. The compounds used were (1) SKS-30A, 100 g; sulfur, 2.2 g; MBTS, 1.6 g; DPG, 1.0 g; zinc oxide, 50 g; antioxidant Neozone D (PBNA), 1.7 g. The filled compounds contained 35 g of channel black, silica gel or chalk. In the compounds containing carbon black 8 g of Kapol were also added. (2) SKB, 100 g; sulfur, 1.5 g; Rubrax (an asphalt), 5 g; stearic acid, 2.5 g. The filled compounds contained 60 g of gas black.

The rubber compounds were prepared by the S. V. Lebedev. VNIISK. They differed from each other by the time of vulcanization at 138° C. The time in minutes is shown on the curves of experimental data. The samples were not subjected to any prior deformation before measurement. During the process of measurement the samples were stretched at a rate of 100% per second until breaking occurred.

The method of measurement, treatment of data and experimental assembly are described in other papers[1–3].

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the experiments are given in terms of the functions: $\sigma_0 = f_1(\lambda)$; $A = f_2(\lambda)$; $\Delta t = f_3(\lambda)$; $\Delta t = f_4(A)$; where σ_0 = stress referred to original cross section of sample, in kg/cm², $\lambda = \frac{L}{L_0}$ = relative elongation, A = specific work of deformation in cal/cm³, Δt = rise in temperature of sample in ° C.

1. Gum rubber compounds.—Figure 1 gives the data for gum compounds of SKS-30A with vulcanization times of 10, 20, 30, 40 and 50 minutes. For clarity the curves are displaced along the abscissa. As can be seen from the stress-strain diagram (Figure 1a) the compounds differ slightly from each other in stiffness and their tensile strength is not high. The maximum stress and elongation were observed for rubbers vulcanized 10 minutes; $\sigma_0 \simeq 37$ kg/cm², $\lambda \simeq 6$.

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for Rubber Chemistry and Technology from *Zhur. Tekh. Fiz.* **27**, 2303–2306 (1957).

The values were 20–25% less for the other compounds. The work of stretching, A, as a function of the degree of stretching, λ, is represented by similar parabolic functions (Figure 1b). The curve for the rubber vulcanized 10 minutes is the steepest but even for this rubber the maximum work is about 2 cal/cm³, a low value of work of stretching. The self heating of the rubbers is not large. At the moment of breaking it is from 4 to 6.2° C (Figure 1c).

At first glance the functions $A = f_2(\lambda)$ and $\Delta t = f_3(\lambda)$ appear to be very similar. This apparent similarity is shown to be a true similarity by quantitative comparison of the values (Figure 1d). The heating increases linearly with the work of stretching up to the breaking point as shown by the function, Δt

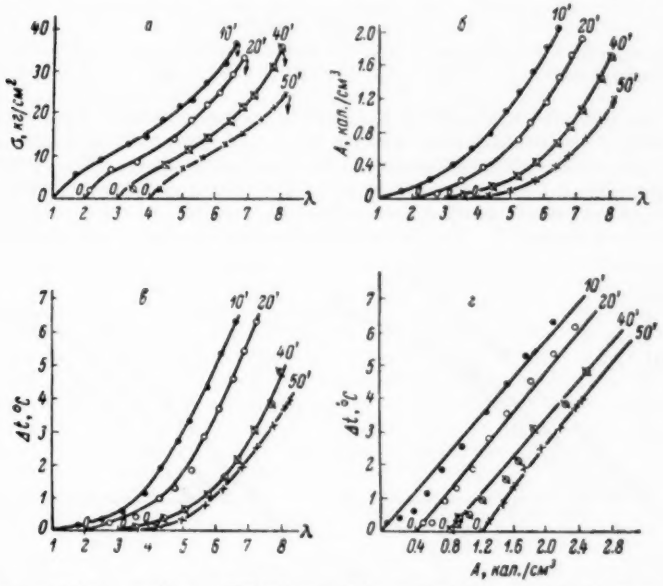

FIG. 1.—Adiabatic stretching of SKS-30A gum rubber compounds. Upper left (a)—Stress-strain diagram; upper right (b)—Specific work of deformation as a function of degree of stretching; lower left (c)—Increase of temperature as a function of degree of stretching; lower right (d)—Heating as a function of specific work of stretching. Abscissa for d; A, cal/cm³. Ordinates: for a; σ, kg/cm²; for b; A, cal/cm³.

$= f_4(A)$. The slopes of the straight lines are equal and correspond to the heat capacity $C \simeq 0.3$ cal/cm³/deg. All of this demonstrates the kinetic character of elastic forces up to break by stretching. Similar regularities were observed on gum vulcanizates of SKB.

2. Filled compounds.—On the addition of fillers to the compounds the elastic properties of the vulcanizates of SKS-30A and SKB change markedly as can be seen from the data in Table I for rubber compounds of maximum stiffness. For example, stress, σ_6, at $\lambda = 4$ (300% modulus) in filled rubbers is 2 to 4 times larger than for gum compounds. Accordingly there is an increase in the work of stretching and in the heating. Thus, at the moment of break of compounds of SKS-30A, $A \simeq 7.5$ cal/cm³ for carbon black loading, 2.8 cal/cm³ for chalk loading and 5.7 cal/cm³ for silica gel loading. The corresponding tem-

TABLE I

THERMOELASTIC CHARACTERISTICS OF RUBBER COMPOUNDS ON ADIABATIC STRETCHING TO BREAK

Filler content	At $\lambda = 4$			At the moment of break			
	σ_0, kg/cm²	A, cal/cm³	Δt, ° C	σ_0, kg/cm²	A, cal/cm³		Δt, ° C
Compounds of SKS-30A							
Gum compound	16	0.6	1.5	36	6.5	2.0	6.2
Channel black 35 parts	52	2	6	82	7.2	7.5	14
Silica gel 35 parts	50	1.8	5	80	6.5	5.7	13
Chalk 35 parts	30	1.2	2.4	45	5.7	2.8	6.4
Compounds of SKB							
Gum compound	9	0.37	0.78	24	7.4	1.6	3.1
Gas black 60 parts	42	2.3	4.6	80	5.6	3.4	6.2

perature rises are 14, 6.4 and 13° C. The greatest work of stretching results in the highest temperature rise. Figures 2a, b, c, d quantitatively compare the heat and work of deformation for all the filled compounds. The curves are displaced along the abscissa for clarity. For rubber compounds differing in degree of vulcanization and in the nature of the filler the heating is proportional to the work expended. The slope of the function $\Delta t = f_4(A)$, for most of the

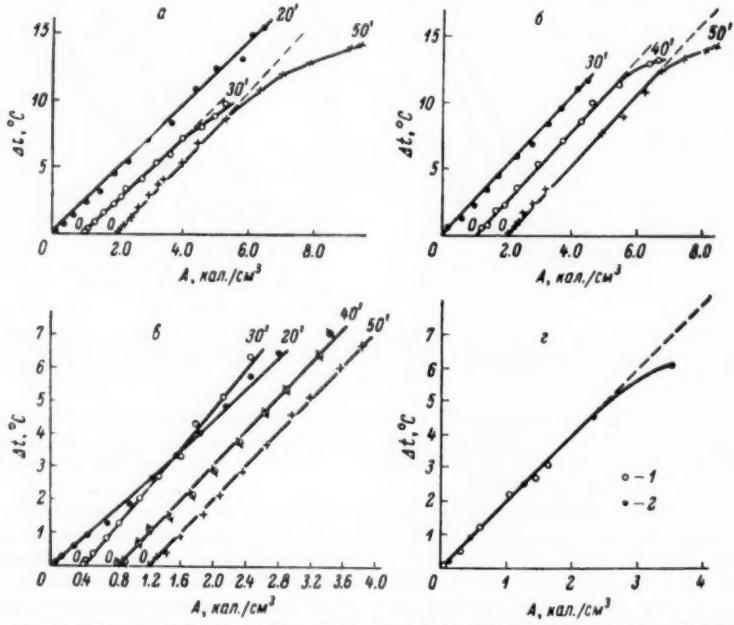

FIG. 2.—Comparison of heating of rubber compounds with the work of adiabatic stretching. SKS-30A compounds: upper left (a)—with channel black, upper right (b)—with silica gel, lower left (c)—with chalk. SKB compounds (d) lower right: *1*—without filler, *2*—with gas black. Abscissa for all curves, A, cal/cm³.

compounds, corresponds to the heat capacity, $C = 0.38$ cal/cm³/deg. An unexplained exception is the chalk filled SKS-30A compounds for which the heat capacities from the function $\Delta t = f_4(A)$ are about 0.43 and 0.33 cal/cm³/deg, respectively.

The SKB compounds with and without filler also heated in accordance with the work of stretching (Figure 2d). The value of the heat capacity for this rubber is $C \simeq 0.5$ cal/cm³/deg.

Thus, practically up to the point of breaking of the rubbers studied, the forces of elasticity are connected with thermal motion of macromolecules. The absence of the crystallization process on stretching the rubbers is apparently due to the irregular structure of the original rubbers. On the addition of active and inactive fillers no new phenomena are observed except that the vulcanizates with active fillers possess the greatest stiffness in comparison with others in a series and there is observed a delayed heating at high elongations; a nonlinearity in the function $\Delta t = f_4(A)$, before break. This deviation from linearity was shown by special experiments not to be due to heat losses or other measurement errors. This indicates the beginning of degeneration of elastic properties of vulcanizates, the appearance of the properties characteristic of rigid bodies. The delayed heat evolution is a result of the superposition of the process of "internal heating" (rigid bodies cool on stretching) on the heating by stretching of materials which continue to be highly elastic.

At high elongations the possibility of change of form of macromolecules by rotation of molecular links of chains around single bonds no longer exists. Thus, the rotational bending of macromolecules (a necessary condition for high elasticity) is lost to a considerable degree. The nature of the thermal motion is determined by the high orientation of the chains. Evidently a high degree of stretching is accompanied not only by the disappearance, in some rubbers, of the convoluted configuration isomers[4], but by deformation of valence angles by change in interatomic and intermolecular distances; in other words by a decrease in density of the material. As a result, part of the work of deformation is consumed by increasing the potential energy of the substance and less heat is evolved.

CONCLUSIONS

1. The stretching of vulcanizates of SKS-30A and SKB before break accompanied by the generation of heat equivalent to the work of stretching indicates the kinetic nature of the elastic forces in these vulcanizates.

2. Change in the degree of vulcanization of the compound and the addition of fillers leads only to a change in the modulus of elasticity of the rubber compound. The rules of conversion of work into heat do not change. The absence of crystallization processes even at high elongation ($\lambda = 6 - 7.5$) is evidently a result of the irregular structure of the hydrocarbon skeleton of the original rubbers, SKS-30A and SKB.

3. For rubbers containing active fillers (channel black and silica gel) and obtained by optimum vulcanization, there is observed a decrease in heat evolution caused by hardening of the material in the region of high elongation just before break.

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THERMOELASTIC PHENOMENA IN NATURAL RUBBER COMPOUNDS DURING CYCLIC DEFORMATION *

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The thermoelastic properties of natural rubber compounds were studied during the stretching-relaxation cycle using the method of adiabatic stretching. The speed of deformation used was 100% per second. The compounds differed from each other by the time of vulcanization and by the fillers used.

It was shown that in the first stages of stretching, the heat generated is equivalent to the work of stretching. Further deformation leads to reversible generation of surplus heat connected with crystallization. The beginning of crystallization of rubber compounds depends on the time of vulcanization and the nature of the filler.

The analysis of the thermomechanical behavior of rubbers stretched under adiabatic conditions (S_0 is constant) shows the following relation between the work of deformation, A, and the change of temperature of the sample, Δt:

$$A \simeq \Delta U + \bar{c}(\Delta t)_{S_0} \tag{1a}$$

where ΔU is the change of internal energy resulting from the rearrangement of macromolecules into the ordered condition, and $\bar{c}$ is the mean value of the heat capacity of the rubber. A, ΔU and $\bar{c}$ refer to the original dimensions of the rubber sample.

It was shown[1,2] that $\Delta U \simeq 0$ for the stretching of non-crystallizing rubber. $\Delta U < 0$ for the stretching of crystallizing rubbers and the heat of deformation, $\bar{c}(\Delta t)_{S_0}$, is a few times greater than work of external force, A. When $U = 0$ the temperature rise of rubber stretched adiabatically is obviously,

$$\Delta t = A/\bar{c} \tag{1b}$$

The purpose of the present experiments is to study (a) the laws governing the conversion of work into heat during cyclic deformation of natural rubber at high rates of deformation and (*b*) the differences in thermoelastic properties of rubber compounds resulting from differences in degree of vulcanization and in the nature of the fillers used.

For experimental testing, natural rubber compounds varying in degree of vulcanization were used. Both gum compounds and compounds containing channel black, silica gel or chalk were studied. The gum compounds contained 100 g smoked sheet rubber, 3 g sulfur, 0.7 g MBT, 5 g zinc oxide, 1.5 g Neozone (PBNA) and 0.5 g stearic acid. The filled rubber compounds contained 100 g smoked sheet rubber, 3 g sulfur, 30 g filler, 0.7 g MBT, 5 g zinc oxide, 1.0 g PBNA, 2.0 g stearic acid and 5.0 g Rubrax (an asphalt). Vulcanization was

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for RUBBER CHEMISTRY AND TECHNOLOGY from *Zhur. Tekh. Fiz.* **27**, 2307–1313 (1957).

carried out at 143°. The time of cure in minutes is shown on the experimental curves. The rubber samples were obtained from the S. V. Lebedev VNIISK. The rate of deformation used was 100% per second. Special apparatus was made which permitted the measurement, with the help of an eight channel oscillograph, of the force, F, the degree of elongation, λ, and the change in temperature of the sample, Δt, as a function of time. The work and the heat

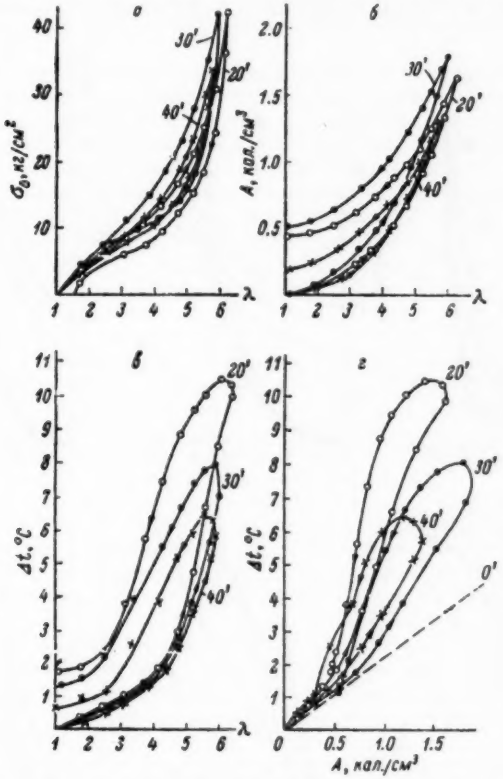

FIG. 1.—Adiabatic stretching of natural rubber gum compounds. a—Stress-strain diagram; b—Dependence of specific work of deformation on the elongation; c—Temperature rise as a function of elongation; d—Temperature rise as a function of specific work of deformation. Abscissa; a—λ; b—λ; c—λ; d—A, cal/cm³. Ordinate; a—σ_0 kg/cm²; b—A, cal/cm³; c—Δt, ° C; d—Δt, ° C.

capacity were determined with a maximum error of ±8%. Measurements were made at room temperature during the stretching-relaxation cycle. Before measurement calibration of each sample was made to determine $\lambda = f(l)$ (l) is the distance between the clamps of the machine). The sample was first stretched a few times to 600–500% elongation and then heated in a thermostated oven to 85–88°. After calibration, the sample was repeatedly heated and cooled to room temperature and finally assembled in the apparatus for making the measurements.

The description of the experimental apparatus, the measurement procedure and the method of analysis of data using Equations (1a) and (1b) are given in the literature[1-3].

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental data in Figures 1 and 2 show the following functions: $\sigma_0 = f_1(\lambda)$; $A = f_2(\lambda)$; $\Delta t = f_3(\lambda)$; $\Delta t = f_4(A)$; where σ_0 = specific force based

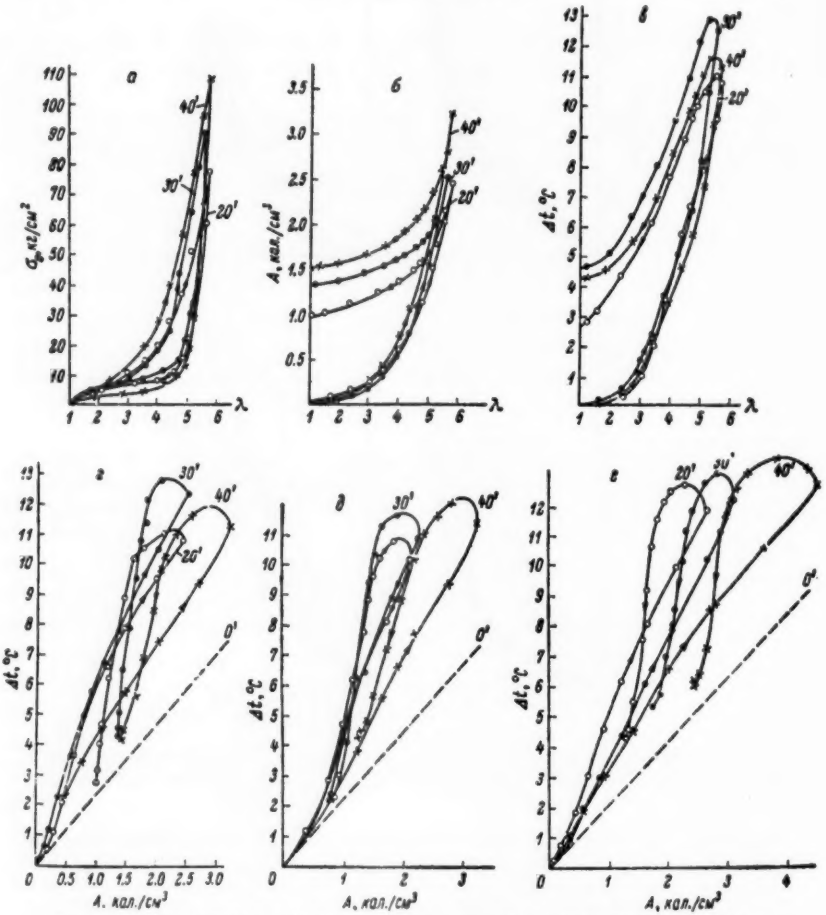

FIG. 2.—Adiabatic stretching of filled natural rubber compounds. Rubbers with channel black: *a*—Stress-strain diagram; *b*—Dependence of specific work of deformation on the elongation; *c*—Temperature rise as a function of elongation; *d*—Temperature rise as a function of specific work of deformation. Rubbers with silica gel: *e*—Temperature rise as a function of specific work of deformation. Rubbers with chalk: *f*—Temperature rise as a function of specific work of deformation. Abscissa: *a*—λ; *b*—λ; *c*—λ; *d*—*A*, cal/cm³; *e*—*A*, cal/cm³, *f*—*A*, cal/cm³. Ordinates: *a*—σ_0, kg/cm²; *b*—*A*, cal/cm³; *c*—Δt, °C; *d*—Δt, °C; *e*—Δt, °C; *f*—Δt, °C.

on original cross section of sample, in kg/cm²; $\lambda = L/L_0$ = relative elongation of a homogeneous part of the sample; A = specific work of deformation in cal/cm³; Δt = change of temperature of sample, °C.

1. Gum rubber compounds (NR).—Gum rubber compounds, NR20, NR30 and NR40, vulcanized for 20, 30 and 40 minutes, respectively, were studied. From the stress-strain curve (Figure 1a) it is seen that increase in time of cure did not produce a steady increase in the modulus of elasticity. The stiffest compound was NR30, with 30 minute cure. NR20 had a large residual elongation—50%.

On our apparatus the direction of deformation is automatically reversed at a definite pre-established distance between the clamps holding the sample. For different samples this does not always give exactly the same maximum elongation. In the calculations these differences can not change the conclusions resulting from comparative data pertaining to different samples.

Stress-strain diagrams for all the compounds are similar (Figure 1a). They differ from each other by the area of the hysteresis loop, and accordingly by the work, A_H, which went into the irreversible generation of heat at the end of the cycle. For example, at $\lambda \simeq 6$ for NR30, the work of deformation, $A = 1.75$ cal/cm³, $A_H = 0.5$ cal/cm³. For compounds NR20 and NR40 the corresponding values are noticeably less.

Heating of samples occurs most intensely after 3–4 fold elongation (Figure 1c). Maximum heating was 6, 7 and 9°, respectively, for NR40, NR30 and NR20. Relaxation of the sample does not immediately result in a lower temperature. For a period of time the process which developed heat continues and only after the completion of this process does the temperature start to fall. Cooling on relaxation proceeds more slowly than heating on stretching. The area of this peculiar hysteresis loop is largest for NR20. Residual temperature rise at the end of the cycle was 0.5, 1.1 and 1.8°, respectively, for NR40, NR30 and NR20 (Figure 1c). Correction for non-identical maximum elongation of samples produced little change in these values.

In Figure 1d is shown the heat effect, Δt, as a function of work of deformation, A. The broken line, 00′, represents the heat effect of an amorphous rubber, calculated by Equation (1b). The effect of mixing of rubber with fillers and other components as well as the effect of degree of vulcanization results in changes in the heat capacity[4] of no more than 10–20%. Therefore, in the approximate calculations with Equation (1b) the value of 0.45 cal/cm³/deg (the value for smoked sheet) was used. On the initial portion of the plot of the function $\Delta t = f_4(A)$ the points are a little higher than the line 00′. The deviation is small and can be explained by experimental error. At higher values of the function, there was observed an excess of heat in comparison with the work of deformation, which is evidently connected with the start of crystallization. The beginning of evolution of the heat of crystallization corresponds to the following values of work and elongation: NR20—$A \simeq 0.5$ cal/cm³, $\lambda \simeq 4.5$; NR30—$A \simeq 0.8$ cal/cm³, $\lambda \simeq 5$; NR40—$A \simeq 0.6$ cal/cm³, $\lambda \simeq 4.5$. From these figures it can be seen that the rubber compound with the highest modulus (NR30) begins to crystallize later than in others.

The processes of crystallization and destruction of crystalline phase proceed at such rates that their progress is greatly retarded. This leads to the lack of coincidence of the stretching and relaxation branches of the function $\Delta t = f_4(A)$ as shown in Figure 1d.

2. Rubber compounds containing fillers.—Figure 2 shows the data for com-

pounds containing channel black, KSR20, KSR30 and KSR40. The presence of the active filler in the compound increases the modulus.

The stress-strain curve becomes very steep (Figure 2a). Maximum modulus occurs in KSR40 (40 minute cure). At $\lambda \simeq 5.5$, $\sigma_0 \simeq 110$ kg/cm^2, $A \simeq 3.2$ cal/cm^3 and the mechanical loss per cycle, $A_H \simeq 1.5$ cal/cm^3 (Figure 2b). The corresponding values for gum compounds are one-half to one-third as great.

Compounds containing silica gel (SR20, SR30, SR40) and chalk (MR20, MR30, MR40) have a lower modulus than the carbon black vulcanizates. The sharp rise in the stress-strain curve for these compounds is shifted to a higher value of λ. In these series the highest modulus occurs with SR40 and MR30. At $\lambda \simeq 5.5$, $\sigma_0 = 70$–80 kg/cm^2 for both compounds. The hysteresis is large, like that of the carbon black compounds. For SR40, A_H 1.3 cal/cm^3 and for MR30, $A_H \simeq 1.7$ cal/cm^3. The greatest mechanical loss, $A_H \simeq 2.5$ cal/cm^3 was obtained with MR40.

The greatest heating of the carbon black vulcanizates occurred after $\lambda \simeq 2.5$ (Figure 2c). Samples stretched 5.5 fold heated 11–13° In spite of the fact that KSR40 was stretched the most, the greatest residual heating (4.5°) was observed with KSR30.

The process of self-heating of carbon black vulcanizates and of rubber compounds containing silica gel or chalk appears to be substantially the same.

In Figure 2d, the temperature rise of black vulcanizates is given as a function of the work of stretching. It can be seen that the carbon black not only increases the modulus but also promotes crystallization on stretching. One can see that the crystallization process occurs practically at the beginning of the stretching ($A \simeq 0.2$ cal/cm^3, $\lambda = 1.8$–2.5). It is also characteristic that the compounds with the high modulus of elasticity crystallize less than the others in a series.

Figures 2 e,f show the relationship between work of deformation and temperature rise for rubber compounds containing silica gel (SR) and chalk (MR). The initial portion of the function $\Delta t = f_4(A)$, is located near the straight line 00′ which characterizes thermoelastic behavior of non-crystallizing rubbers. The energy change produced by crystallization starts, for SR20, SR30 and SR40, at $A \simeq 0.4$, 0.5 and 0.6 cal/cm^3 ($\lambda \simeq 3.5$, 3.6 and 3.7) and for MR, at $A = 0.1$–0.2 cal/cm^3 ($\lambda = 2.0$–2.5). Compound SR40 possesses the highest modulus in the SR series and shows the least crystallization. In the chalk series crystallization occurs later the longer the vulcanization time. MR30 with the highest modulus is not distinctly different from the other compounds.

The transition from stretching to relaxation does not lead to immediate cooling. The progress of crystallization and melting is so slow that there is no coincidence between the stretching and relaxation portions of the function $\Delta t = f_4(A)$. In fact they even cross each other toward the end of the cycle, except in the case of the silica gel compounds.

The irreversibility of the process connected with the development of crystals is very large. Therefore, fusion is accompannied by very little useful work and the relaxation branch of the curve $\Delta t = f_4(A)$ drops sharply. In general, with all filled compounds, the points at the end of the cycle are located above the line 00′ representing Equation (1b). The reason for this will be discussed later.

REMARKS ON THE METHOD

1. From Figure 1d it is evident that the points on the curve $\Delta t = f_4(A)$ near the end of the relaxation cycle lie on the line 00′, within experimental

error. The equality between the work for the complete deformation cycle and the heat evolved irreversibly indicates that the heat losses were low and did not substantially affect the measured values. Thus, at deformation rates of 100% per second, adiabatic stretching can be accomplished without taking special measures such as the use of vacuum chambers, samples of large cross section, etc.

2. From Figures 2d,e,f, it can be seen that for filled compounds the values of the function $\Delta t = f_4(A)$ at the end of the cycle are located above the line 00′. The deviation is partly due to the fact that the heat capacity of filled vulcanizates is less than 0.45 cal/cm³/deg. In this case the line 00′ should have a greater slope. However, the main cause for deviation is error in determining the elongation of a homogeneous portion of sample which results in an error in the calculation of the work of deformation.

In these experiments the distance between the clamps was automatically recorded by means of the eight channel oscillograph. The determination of the degree of elongation, λ, is made from the calibration curve, $\lambda = f(l)$. As can be seen from Figure 3, there is not a well defined relation between λ and l

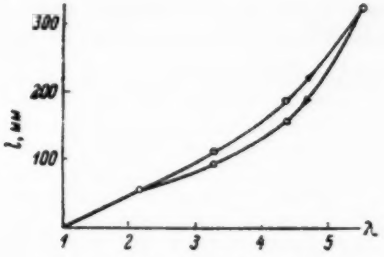

FIG. 3.—Abscissa: λ. Ordinate: l, mm.

under cyclic deformation conditions. With an increase in the rate of deformation the loop becomes larger. If the stretching branch of the curve $\lambda = f(l)$ does not change location noticeably then the relaxation branch lies below it, as a rule. This is most noticeable with filled compounds.

The calibration curve $\lambda = f(l)$ was photographed at a mean speed of deformation of 4% per second and measurements were made at 25 times this rate (100% per second). Therefore the work of deformation in the relaxation cycle was overestimated. Correspondingly the relaxation branch of the curve $\Delta t = f_3(\lambda)$ is displaced toward lower elongations.

The errors in the determination of the work of relaxation are systematically accumulated and reach a maximum value at the end of the cycle. As a result, the final points on the curve $\Delta t = f_4(A)$ for filled rubbers do not coincide with the line 00′.

The errors shown above make quantitative calculations dificult. Therefore, in later work we changed to direct automatic recording of elongation of homogeneous portions of sample. For this we used a specially developed extensometer[5].

CONCLUSIONS

1. The initial stages of stretching of natural rubber gum compounds ($\lambda \leqq 4.5$) and of filled compounds (λ = 1.8–4) are characterized by liberation

of heat equivalent to the work of deformation according to Equation (1b). Further deformation takes place with liberation of surplus heat caused by crystallization of the rubber. The relation between the work of deformation and the heat effect is given by Equation (1a)

2. The beginning of crystallization and its degree at a given elongation depend on the degree of vulcanization and on the nature of the dispersed fillers.

The rubbers with the highest modulus crystallize the poorest.

Active fillers such as channel black promote crystallization to a greater degree than silica gel and chalk.

3. A rate of deformation of 100% per second assures adiabatic conditions without taking special measures.

4. It was determined that errors in the quantitative analysis of the process of adiabatic stretching of rubbers result from lack of knowledge of the true heat capacity of the compound and especially from inaccuracy of measurement of elongation during the relaxation cycle.

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DEPENDENCE OF DIELECTRIC RELAXATION SPECTRUM OF RUBBER ON STRETCHING *

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INTRODUCTION

The dielectric relaxation spectra of high polymers, i.e., the dielectric constant and loss angle as functions of temperature and frequency, will differ, depending on whether the material is in the oriented or unoriented state. This dependence of the dielectric spectrum on elongation has already been observed in somewhat rigid high polymers, such as polyvinyl chloride, polyamides, etc. The changes taking place follow certain mathematical principles[1].

It was important also to determine to what extent the dielectric spectrum of elastomers changes as a function of the state of elongation, and whether such changes obey the same laws.

The dielectric behavior of a material appears to be of interest primarily only for practical applications in the electrical industries. But the adoption of an essentially broader viewpoint provided the impetus for the cited experiments: the dielectric spectrum displays features that parallel, to a considerable extent, those of the mechanical spectrum. If, then, the thawing of a molecular mechanism can be recognized from the dielectric spectrum as the maximum of the loss angle, this structural mechanism must perforce also be effective mechanically in approximately the same temperature or frequency range[2]. In other words: changes in the dielectric spectrum indicate changes in mechanical behavior.

Actually, many high polymers can be improved by stretching; for example polystyrene, which is very brittle in the unoriented state, becomes flexible when stretched[3]. A polyamide, like many other substances, acquires its highly desirable mechanical properties only after it has been oriented[4]. Viewed from this angle, examination of the dielectric characteristics as functions of stretching takes on considerably more interest.

As a matter of fact, we were able to show, for almost all the high polymers tested, that not only do the loss angle maxima found in the unstretched state vary as to height and, sometimes, position, but that even entirely new maxima may appear[5]. This means that orientation gives rise to new molecular mechanisms which, because of the relationship between mechanical and dielectric behavior, can also eventually reduce the brittleness of the material and help relieve additional critical stress conditions during mechanical loading of this material.

It is known that the elastic moduli of rubber are dependent on the orientation, even in the static state. Hooke's law concerning the linear relationship between stress and strain with constant E modulus is valid only for smaller elongations; the stress-strain diagram shows an S-shaped curve. Also known

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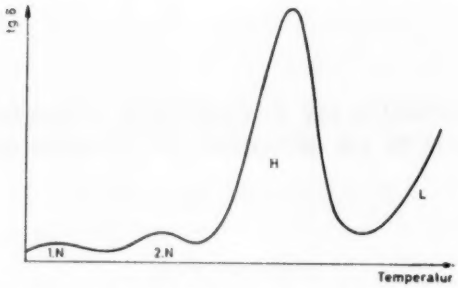

FIG. 1.—Principal course of tan δ as a function of the temperature. H = primary maximum; N = secondary maxima; L = conductivity.

is the fact that with high degrees of elongation crystalline regions are formed[6]. From this standpoint, too, it seemed interesting to see what additional information might be gathered for rubber from the alteration of the dielectric spectrum as a function of the elongation.

COMMENTS ON DIELECTRIC SPECTRUM

Comprehensive information can be secured through dielectric investigation if one knows the real part ϵ' or the imaginary part ϵ'' of the dielectric constant ϵ^* over a broad range of temperature and frequency[7]. Since investigations extending over a wide frequency range are considerably more demanding, generally the temperature behavior for a closely-spaced series of points is examined. Furthermore, the probability of reaching certain conclusions is quite high, if, instead of the difficultly measurable and not too sensitive change in the components ϵ' and ϵ'' of the dielectric constants, the ratio $\epsilon''/\epsilon' = \tan\delta$, that is, the tangent of the dielectric loss angle, is measured. For high polymers, tan δ in the softening region shows a sharply defined maximum, as long as the material is polar. Almost all high polymers, however, will display weaker secondary maxima when lower temperatures are reached.

For rubber the primary maximum is essentially accessible. The one sec-

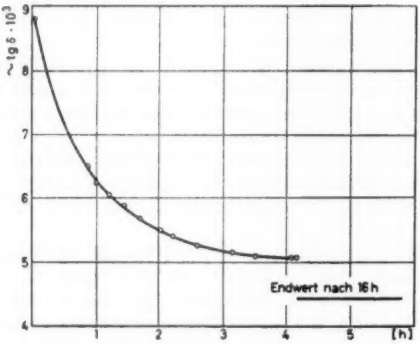

FIG. 2.—Time dependence of the loss angle for a rubber membrane drying over P_2O_5. End value obtained after 16 hours. Ordinate: Hours.

ondary chain maximum, present in all the substances investigated so far, is doubtless detectable in several curves, especially at highest frequencies, yet it obviously still lies at considerably lower temperatures than those used here.

Pure raw rubber is practically nonpolar and would show only a very weakly delineated primary maximum[2]. Impurities, e.g., protein components, can also cause small maxima. Vucanizates, however, possess, in the chemically incorporated sulfur crosslinks, strong partial moments that are oriented in the field according to mobility[8]. For this reason the experiments were conducted with vulcanized samples.

There was another reason for using vulcanized test pieces: A material can be tested in the oriented state only when it can be held for a rather long time in this condition. An uncured sample would relax strongly, as is known, with a coincident, continual change in the average orientation of the chains.

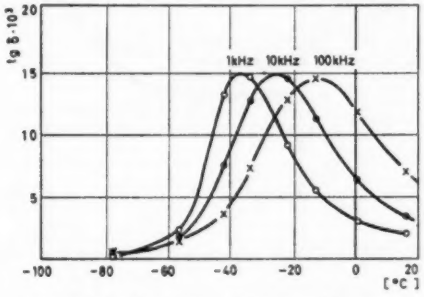

FIG. 3.—Loss angle of unstretched rubber film as a function of the temperature. $kHz = 1000$ cps.

APPARATUS AND TEST PIECES; RESULTS

To carry out the dielectric measurements in the stretched state the rubber film is stretched between two jaws to keep its length constant. The electrode was provided by conductive lacquer (furnished by the firm Heraeus), selected so that the vulcanizate could not be affected by the solvent in the lacquer. Moisture in the condenser was kept at zero by means of phosphorus pentoxide. A definite moisture content, e.g., complete dryness, is absolutely necessary for comparative measurements. The value of $\tan \delta$ (as, besides, the dispersion situation) is essentially dependent on the water content (cf. Figure 2).

For the actual measurement, a Wirk-type measurement bridge was used, described in detail elsewhere[9]. The frequency range of the bridge was 300 cps $\cdots$420,000 cps, and the temperature interval used was from $-120°$ to $+20°$ C. It was not necessary to test at temperatures above $+20°$ with the low sulfur content of the vulcanizates (1 to 2%). since the chief dispersion region lies between $-20°$ and $+20°$. The rubber films used (natural rubber) contained no fillers, according to the manufacturer, and were vulcanized at $+120°$ to 130° C.

The dielectric behavior of natural rubber gum compound as a function of the temperature and the degree of vulcanization has long been known[10]. These are the measurements through which the applicability and validity of the dipole theory, developed for small molecules (normal liquids), was proved for high polymers[8,11]. Evaluation of these measurements shows that the partial mo-

ment at the chemically bound sulfur atom is significant for the dielectric behavior. This partial moment can be accurately reckoned as having the same magnitude as that possessed by thioethers of law molecular weight[5].

Figure 3 shows the loss angle of the unoriented rubber film as a function of the temperature, for 1000, 10,000, and 100,000 cps. The maxima shift, with rising frequencies, toward the higher temperatures, which is as it should be. The height of the maxima declines as the frequency increases.

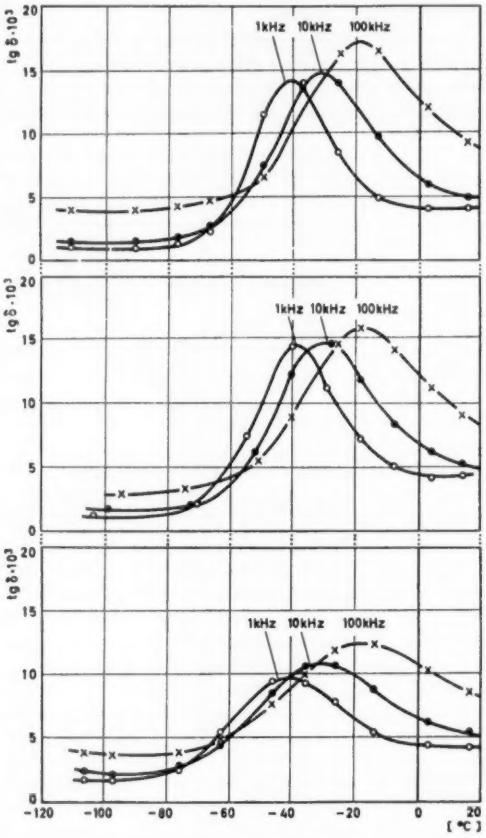

FIG. 4.—The same film as in Figure 3, elongated at 60% and clamped.

FIG. 5.—As in Figure 4, 200% elongation.

FIG. 6.—As in Figure 4, 400% elongation.

Figures 4, 5, and 6 represent corresponding curves for stretched films elongated at 60, 200 and 400%. Here, too, the loss angle maxima are displaced toward more elevated temperatures as the frequency is increased. In contrast to the unstretched sample, however, the maxima peaks go higher along with the frequency.

From the curves in Figures 7, 8 and 9, giving results of tests with stretched and unstretched samples, each at one frequency, it is evident that the loss angle changes with elongation. Even at elongations of 60% the maxima will

shift toward lower temperatures for all investigated frequencies, to about the same extent, $8 \pm 1°$ C, as compared to the unoriented sample. With further elongation the temperature status of the maxima remains practically constant. Initially their height variations are different. Whereas these drop slightly for the first stage of 0 to 60% elongation in the curves at 1000 cps, the 10,000 cps curves already show an increase that is further heightened in the curves for

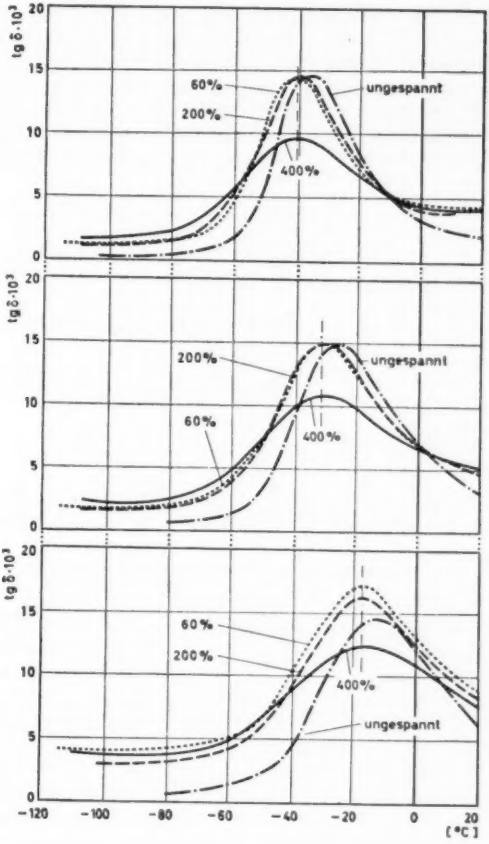

FIG. 7.—Curves for 1000 cps assembled from Figures 3 to 6. Ungespannt = unstretched.

FIG. 8.—As in Figure 7, for 10,000 cps.

FIG. 9.—As in Figure 7, for 100,000 cps.

100,000 cps. When extension is increased to 200% the modification is but slight. However, at 400% extension there is, in every case, a strong depression of the maxima. Generally the half-value spread shows a growth with rising of the maximum peak.

It is furthermore striking that extended strips display greater losses (tan δ values) at lower temperatures, e.g., $-100°$ C, especially noticeable once again at 100,000 cps.

To complete the picture, the double refraction of the rubber film as a func-

tion of the elongation was measured (Figure 10), with a polarizing microscope manufactured by Leitz and with a Bereck compensator, the thickness being determined at 23° C. After first rising in linear fashion, the curve bends upward, at over 100% stretch, in the known manner and then turns the other way at a break occurring in the vicinity of 350%.

DISCUSSION

Let us consider first the initial shifting of the loss angle maxima at slight extensions, toward lower temperatures: Earlier measurements had already demonstrated, with other amorphous or rigid high polymers (polyvinyl chloride, polystyrene, polyvinyl alcohol)[1], the displacement towards lower temperatures of the rise to the primary maximum when the samples were extended. The principal dispersion region was at that time not thoroughly investigated, since the test pieces shriveled up upon approaching the softening point. Even clamp-

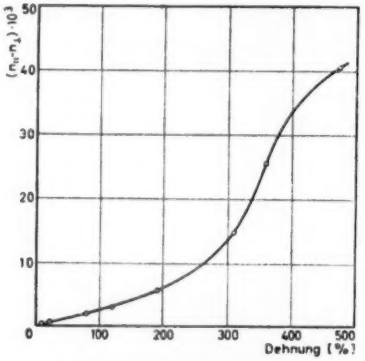

FIG. 10.—Double refraction of rubber membrane as a function of the elongation. Dehnung = elongation.

ing of the samples would not have prevented disorientation of the chains. For this test, as in the present case, crosslinked materials must be used. From the shift in position of the rise, however, it was concluded, even from the former measurements, that the chief dispersion area is displaced in the direction of lower temperatures due to stretching. Such a conclusion is unqeuivocally confirmed by the tests we conducted with rubber.

An oriented material thus obviously possesses a lower freezing point. Activation of the change-in-position mechanism requires less thermal energy, since the (frozen) rubber-elastic tension facilitates the appearance of the thermal place-exchange. The measurements also confirm earlier experiments with polystyrene and polyvinyl chloride with respect to the relations of freezing point and orientation[12]. For example, in highly oriented polyvinyl chloride the temperature of incipient shrinkage phenomena is more than 20° C lower than the point at which softening of the unoriented material begins.

The decrease in height of the peaks at considerable extensions (400%) is also easily explained: It is caused by crystallization of the rubber at high orientations. The dipoles incorporated in the crystallites become stabilized and hence do not contribute to the dipole mechanism anymore.

Analysis of the double refraction shows that the first deviations from linearity commence at about 100% extension. Thiessen and Wittstadt have also determined that double refraction is a function of the temperature[13]. Up to 200% elongation they observed the same course for all temperatures. From then on the curves diverged. From both determinations, it follows that crystallization sets in at about 200% elongation.

A certain approximation of the percentage portion of crystallites might be possible by comparing the areas under the tan δ maxima at 200% and 400% extension, if measurements of tan δ were available in a correspondingly larger frequency range[7]. Such lowerings of the loss angle maxima can also be observed in other high polymers, especially terylene[1].

Difficult to explain is the reversal of the variation in the height of the peaks with rising frequency when there is a stretch whereas, in the unoriented state, the peaks drop slightly and a strong upswing is noted between 1000 and 100,000 cps, even with only 60% elongation.

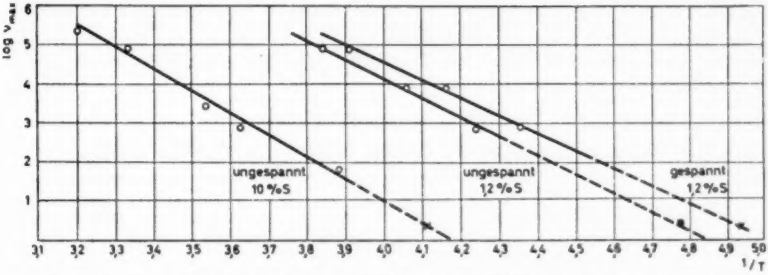

FIG. 11.—Log ν_{max}. plotted against $1/T$ for stretched and unstretched rubber. Extrapolation for unstretched rubber to 2 cps frequency. The values for an unstretched vulcanizate containing 10% sulfur are included. (Values obtained from the measurements of Curtis, MacPherson and Scott).

The theory demands constancy in the height of the peaks, or, with growing half-value breadth, a corresponding decrease[14,9]. Other cases are known from the literature in which a lowering or raising of the maxima is noticed with rise in frequency. However, no quantitative theory has as yet been expounded. It seems to be a general rule, however, that an increase in the maximum of tan δ with the frequency is observable when the chain itself becomes more rigid.

Taking this observation into account, one could conclude that in stretched vulcanizates orientation of the sulfur dipoles is more initimately connected with the chain mobility than in the relaxed, cured samples. To discuss this question reference should be made to the activation values:

By plotting frequencies for the loss angle maximum as a function of the reciprocal absolute temperature, Figure 11, one obtains straight lines the slopes of which give the experimental activation energy ΔE^*. The following holds true for the relaxation time of the observed mechanism: $1/\tau = A \cdot e^{\Delta E^*/RT} = \nu_0 \cdot e^{\Delta G^*/RT}$; $\Delta H^* = \Delta E^* + RT$; $\Delta G^* = \Delta H^* - T\Delta S^*$. τ is connected with the frequency for the tan δ maximum (see Ref. 9 for details).

From the ordinate intersection for $1/T = 0$, or the position of the straight lines in the coordinate net, the activation entropy can be calculated with certain assumptions about the universal frequency. The latter is related to the degrees of freedom of the adjustment mechanism: as the activation entropy

increases, the number of positions in which the group can be arranged will also increase. A stiffening of the chain should therefore lower this number. In fact, the entropies of activation decrease when stretching takes place (see Table I). The division of the socalled free activation enthalpy ΔG^* into enthalpy portion ΔH^* and entropy portion $T\Delta S^*$ was not through extrapolation, but calculation[9]. Of course, one must always bear in mind, with this procedure the error limits for the entropy values are large, to say nothing of the necessity for an assumption about the socalled universal frequency $\nu_0 = kT/h$.

The vulcanizate which was tested contained 1 to 2% bound sulfur, according to the supply firm. A comparison of the loss angle peaks in the unstretched state with measurements made by Curtis and MacPherson[10], for different amounts of combined sulfur, permits estimation of the bound sulfur content as between 1.2% and 1.5%. By using the measurements of the same authors for the activation values of a vulcanizate with 10% sulfur, a definite rise in the activation enthalpy results. The activation entropy for this unextended sample, however, is practically identical with what we found for unstretched rubber containing 1.2% combined sulfur. We evaluated the measurements of the cited authors as to activation values, using the same formulas we used to evaluate our own measurements.

TABLE I

ACTIVATION VALUES OF THE PRINCIPAL MAXIMUM OF VULCANIZATES

	ΔE^*	ΔH^*	ΔG^*	$T\Delta S^*$
Unstretched	22.3	21.7	7.4	14.3
Stretched	20.7	20.1	7.9	12.2
10% S unstretched	26.2	25.6	11	14.5

* In kcal/mole for $T = 300°$ C.

This shows that variation of the concentration of combined sulfur, in contrast to the change caused by elongation, has no noticeable effect on the activation entropy for the sulfur contents investigated. Thereby the conclusion drawn here, from analogy to high polymers which varied in the rigidity of the chains, is upheld, namely that a greater stress involving the chain mobility of stretched samples would be decisive for the course of the tan δ maximum with frequency.

More difficult to explain than the change in the general frequency dependence of the tan δ peaks is the continually appearing increase in the maxima when the curves for the unoriented and the 60% elongated rubber—especially noticeable in the 100,000 cps curve. For this, measurements at high temperatures should have been available, for it is conceivable that the increase was related to an increase in the "background", viz: the residual losses. These residual losses, recognizable in the rise in tan δ values for about $-100°$ C, i.e., outside of the dispersion region, both with respect to frequency and—what was even more strongly noticeable—with extension, probably represent a more general phenomenon, which has not been discussed up to now. The activation straight lines reproduced in Figure 11 permit still another comparison of the dielectric measurements with mechanical investigations.

If one extrapolates the frequency value for the maximum to a frequency of 2 cps, then, there results for the unstretched material, a temperature of the tan δ maximum of $-60°$ C. This is 5° higher than that found by Schmieder

and Wolf[15], using vulcanizates with 1.5% sulfur and less, for the position of the principal mechanical damping maximum. In fact, Thurn[16] has shown that the mechanical maximum for the same mechanism lies several degrees lower than the dielectric maximum, and it can be said that this extrapolation of the dielectric behavior is as valid for the mechanical behavior of rubber as in the case of the two secondary maxima investigated in polyamide[1]. No comparable measurements are available for extended rubber.

SUMMARY

The loss angle of a weakly vulcanized rubber sample, as a function of temperature and frequency, changes as the sample is extended. Even at slight extension the loss angle maximum is depressed and shifts by several degrees to lower temperatures. The results are discussed in relation to earlier investigations of changes in the dielectric spectrum when various other rigid high polymers are stretched. Such experiments are interesting, since the close connection between dielectric and mechanical spectra permits conclusions to be drawn about modifications in mechanical behavior caused by stretching. A new method is presented for obtaining additional quantitative data regarding mechanical behavior in the nonlinear region.

ACKNOWLEDGMENTS

We wish to extend our sincree thanks to: *die Deutsche Kautschuk-Gesellschaft* for furthering this work by supporting the laboratory, and to: *die Deutsche Forschungsgemeinschaft* for the granting of a stipend.

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CIS-TRANS ISOMERIZATION OF NATURAL RUBBER UNDER THE INFLUENCE OF ORGANO–ALUMINUM COMPOUNDS AND TITANIUM TETRACHLORIDE *

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Ziegler catalysts have become of prime importance for synthesis of polymers with regular structure, particularly *cis*-polyisoprene[1–4]. The disruption of the structure of the chain by the formation of *trans* units was, until now, connected only with the influence of the physical and chemical properties of the catalyst on the nature of the addition of the diene monomers during the polymerization process. In the present work it is shown that destruction of regularity of structure can be caused by isomerization of *cis* units in complete polymer chains into *trans* units under the influence of the compounds used for initiating the polymerization process.

Attempts to isomerize natural rubber by means of ultraviolet light and iodine[5] did not give the expected effect. Ferri[6] established for the first time that under the influence of zinc chloride and titanium tetrachloride natural rubber undergoes changes accompanied by disappearence of crystallization on stretching as shown by x-ray structure analysis. On the basis of these results the authors presumed that under the influence of these agents isomerization of *cis* units to *trans* units occurs in the natural rubber chain.

The isomerization of *cis*-1,4 units to *trans* units in polybutadiene by means of ultraviolet light in the presence of organic bromine or sulfur compounds was first accomplished and proved by Golub[7]. The formation of *trans* units in natural rubber under similar conditions was not observed.

The study of the isomerizing effect of $TiCl_4$ and organo-aluminum compounds was conducted by us on solutions of milled natural rubber (NK) in benzene in sealed glass ampoules. The benzene used was dried and distilled over sodium. All work was conducted in an atmosphere of dry argon. Unsaturation and microstructure of the chain was determined on each sample.

The study of microstructure of polyisoprenes was carried out by means of infrared spectra, the relative content of the different configurations of the polymer chain being determined by the absorption in the 800–1000 cm^{-1} region. The method previously developed by one of us[8] was used for this purpose.

The results of the quantitative analysis of the microstructure of the original sample of NK and of samples exposed to the action of isomerizing agents are given in Table I where the amounts of *cis*-1,4, *trans*-1,4, 1,2 and 3,4 configurations are listed, calculated on the basis of the concentration of double bonds, C=C.

From the given data it follows that the components of Ziegler catalysts of polymerization ($TiCl_4$, AlR_3, AlR_2Cl) exert an isomerizing effect on the poly-

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler from *Doklady Akad. Nauk SSSR* 123, 685–687 (1958) for Rubber Chemistry & Technology.

TABLE I

ISOMERIZATION OF NATURAL RUBBER UNDER THE INFLUENCE OF $TiCl_4$ AND ORGANO-ALUMINUM COMPOUNDS AT 90° USING A 2% RUBBER SOLUTION

Sample	Isomerizing agent	Isomerizing agent content, weight % on rubber	Time of reaction, hours	Unsaturation, % of theory	Structure by infrared spectra, %			
					cis-1,4	*trans*-1,4	3,4	1,2
1	—	—	—	99; 99.5	95	3	2	0
2	$TiCl_4$	10	10	86.5; 87	65	33	2	0
3	$TiCl_4$	10	10	84; 85	67	32	1	0
4	$TiCl_4$	10	10	Not determined	68	29	2	1
5	$TiCl_4$	50	10	61.5; 65.1	13	78	6	3
6	$TiCl_4$	10	1	75.4; 72.8	74	21	4	1
7	$TiCl_4$	10	20	68.5; 64.5	44	51	4	1
8	$AlEt_2Cl$	10	10	65; 65.5	58	40	2	0
9	$AlEt_3$	10	10	89; 85.4	59	47	2	2
10	di(2-phenyl-ethyl) ethyl aluminum	10	10	83; 81	69	30	1	0
11	Triisobutyl aluminum	10	10	70; 74	43	54	2	1

mer chain of natural rubber. For example, with titanium tetrachloride it was found that the quantity of *trans* units increases with the concentration of isomerizing agent and with the time of reaction.

The isomerization of polyisoprene discovered by us is clearly illustrated by the curves of Figure 1 showing the infrared absorption bands corresponding to different *cis-trans* contents.

Since the molar absorption coefficient, K, for *cis* units in polyisoprene at $\nu = 839\ cm^{-1}$ is 52 but is 28 for *trans* units at the same wave number, the relative decrease of intensity of absorption bands caused by *cis-trans* configurations (when calculated on the basis of the total concentration of double bonds, C=C)

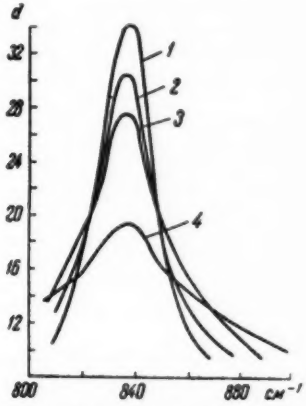
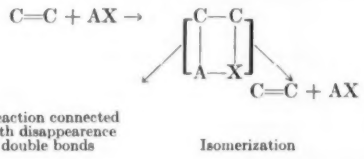


FIG. 1.—The infrared absorption bands for different contents of *cis-trans* configuration in the polymer chain. *1*—Natural rubber (NR): *cis* 95%, *trans* 3%. *2*—Isomerized NR: *cis* 65%, *trans* 33%. *3*—Isomerized NR: *cis* 44%, *trans* 51%. *4*—Isomerized NR: *cis* 13%, *trans* 78%.

is a measure of the decrease of *cis* configuration in the polymer chain and the corresponding increase of *trans* configuration.

The process of isomerization occurring under the influence of the described agents is accompanied by an appreciable decrease in unsaturation of the polymer. A considerable decrease in unsaturation without decrease in solubility of the polymer appears to be due principally to the process of cyclization within the chain as has been reported in one of our papers.

The decrease in unsaturation is connected with the ability of the above compounds to add to the C=C bond. Then there is apparently a stage of formation of an unstable complex capable of decomposing to regenerate the original substance. Isomerization can occur during this intermediate stage:



We established that in the case of ethyl aluminum dichloride natural rubber undergoes secondary changes; the process proceeds to the formation of insoluble high melting amorphous powders. A similar effect was observed when large quantities of $TiCl_4$ were used (100% on the rubber).

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THE IMPORTANCE OF RHEOLOGY IN THE PROCESSING OF RUBBER. 1. RHEOLOGICAL INVESTIGATIONS OF RUBBER SOLUTIONS *

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INTRODUCTION

An important basic problem encountered in the rubber processing industry has always been the finding of a precisely defined and scientific criterion for the different grades of rubber. Of paramount interest are the relations between the molecular weight of the raw or masticated rubber and the physical and chemical properties of the corresponding vulcanizate. From purely practical considerations, in the technology of rubber, preference has been given to investigations of the solid material rather than the corresponding solutions. This has been true, above all, for the entirely empirical Defo value. For many years, in Germany, the Defo value has been the standard not only for the mechanical characteristics required for any practical application, but for the surveillance of all degradative processes as well. This plasticity value, however, will not provide the accurate information necessary for an exact study of energy-consuming mastication processes. A generally valid relationship has not been established between Defo hardness and solution viscosity, or even molecular weight. Thus, because of structural dissimilarities, the viscosity curves for Buna S3 and natural rubber are not identical when their Defo values are the same[1]. In principle, only the following rule holds true: the higher the molecular weight of the rubber, the greater will be its Defo hardness and solution viscosity. But the Defo value, like all measurements of solid rubber, has the advantage that measurement times are substantially shorter than those for the corresponding solutions.

But knowledge of the exact molecular weights of the various grades of rubber ceases to be of merely theoretical importance since the further development of rubber technology depends essentially on how rapidly precise methods of scientific investigation can come into play. Mullins[2] has already discovered that the initial molecular weight of unvulcanized, masticated rubber will affect the degree of crosslinking and hence the swelling, tensile, and elongation properties of the vulcanizates. Yurshenko and Maleyev[3], too, came to the conclusion—important for the theory and practice of rubber reinforcement—that the time required for the adsorption of blacks by high polymers increases with rise in molecular weight.

The molecular weight of rubber is determined by the number of chain segments in the unsaturated C_5H_8 groups. Since rubber is a high polymer, its individual molecules never have the same chain length, but constitute, rather,

* Translated for Rubber Chemistry and Technology by G. Leuca from *Gummi und Asbest-Plastische Massen*, Vol. 11, pages 251–258, May, 1958.

a polymer-homolog mixture of chains of varying lengths. As a consequence, each molecular weight determination furnishes only one mean value. For a more exact characterization, the chain length distribution, or polymolecularity, should also be known. The properties of a rubber are largely dependent on these two values, average molecular weight and polymolecularity. Their knowledge permits statements that are considerably more accurate than those based on conventional mechanical tests. Compared to the latter, exact determinations of molecular weight and chain length distribution, e.g., by fractionation, require a relatively long time. The present work is an attempt to show how rheology can be utilized in the rubber-processing industry to obtain, from an easily and quickly plotted flow curve, a value dependent on the weight-average molecular weight, and a numerical value for the polymolecularity as well.

THEORY

Because of the macromolecular nature of rubber, its solutions exhibit colloidal characteristics. Viscosity is affected greatly by the chain length of the dissolved macromolecules. In solutions of equal concentration the viscosity climbs as the molecule size increases. When the rubber is processed, degradative reactions take place, also recognizable through the drop in viscosity. That is why viscosity measurements are indispensable, both in laboratory research and for control of factory processing.

Thus, as long ago as 1904, Axelrod[4] was already conducting viscometric investigations of rubber solutions. While testing the solubility of various types of rubber in benzene, he recognized a typical phenomenon, that a relation existed between the quality of the rubber and the viscosity of its solution, which agrees with practical experiences. Without being able to offer proof, he already based his observations on the connection between viscosity and elasticity on differences in chemical relationships, principally on a higher or lower degree of polymerization of the rubber molecules.

Later, DeVries[5] employed viscosity measurements for practical determinations of the quality of rubbers. Then Fikentscher and Mark[6] investigated the quantitative relation between the viscosity of a rubber solution and its degree of mastication, and the average chain length of its molecues, whereby the molecular weights were determined only indirectly. Similarly Ostwald[7] has also called attention to the practicability of determining molecular weight by measuring the viscosity of solutions of masticated rubber.

Through application of modern rheological techniques it is now possible to state simply, rapidly and directly, i.e., in an absolutely viscometric manner, the weight-average molecular weight and the polymolecularity. One need merely take into account the fact that the viscosity η is a material constant only in the case of Newtonian liquids, e.g., water, hydrocarbons, and solutions of low molecular weight substances. Here the velocity gradient G rises proportionally with the shear stress P, and even with the most varied shear stresses, the same quotient is always obtained:

$$\eta = \frac{P}{G}$$

But even slight amounts of rubber will cause an uncommonly sharp rise in the viscosity of the solvent. This results in deviations from the Newtonian definition of viscosity. Such non-Newtonian liquids display viscosities that depend on the different stresses applied, a phenomenon we refer to as structural

viscosity. Such flow behavior is defined simply by a functional dependence of the shear stress P and velocity gradient G:

$$G = f(P)$$

The viscosity of rubber solutions and other high polymers therefore, is just a function of the shear stress and the velocity gradient. Consequently, a viscosity measurement supplies only a pseudo-viscosity, η' that is dependent on the experimental conditions. Now in order to assess properly the flow characteristics of these fluids which exhibit structural viscosity, it is necessary to plot a so-called "flow curve" for ranges of shear stress and velocity gradient extending over four to six powers of ten.

When the velocity gradients are low, in the η_0 region, and at very high velocity gradients, in the η_∞ domain, such solutions show Newtonian flow, i.e., they have a constant initial and terminal viscosity. The structural viscosity zone lies in between, with an inflection point in the middle of the flow curve. At this point the dropping in viscosity has reached a maximum. Hence the inflection point in the flow curve becomes a critical point, best characterized by the critical velocity gradient $\hat{G}$. Accordingly, the flow curve is S-shaped.

The reasons for this non-Newtonian flow have been reported elsewhere in detail[8]. As a result of the diverse deformabilities of the individual molecular chains, the weight average molecular weight and the polymolecularity have an effect on the shape of the flow curve and its position within the coordinate system.

In contrast to the representation of a curve for flow behavior according to Philippoff[9], what is being accepted more and more nowadays is a new type of flow curve, whereby the apparent (pseudo-) viscosity η' is plotted against the velocity gradient G resulting from each shear stress, in a log-log system of coordinates. Then the regions of η_0 and η_∞, as well as the Newtonian liquids, lie on straight lines parallel to the abscissa, and the inflection point, the critical velocity gradient $\hat{G}$, is halfway between η_0 and η_∞.

As already explained in earlier work[10], the viscosity of a high polymer solution at the inflection point depends purely on the size of the macromolecules. Besides, the critical velocity gradient $\hat{G}$ is independent of the concentration as first established by Umstätter[11] and confirmed by Edelmann[10] in numerous studies. Therefore this value, $\hat{G}$, the velocity gradient at the inflection in the flow curve, becomes a material constant of the dissolved high polymer. Its order of magnitude depends exclusively on the weight average molecular weight of the macromolecular substance. This feature of the flow curve opens up the prospect of determining the molecular weight in an absolutely viscometric manner. In practice, however, knowledge of the precise molecular weight is generally not necessary. Determination of a value dependent on the molecular weight, e.g., $\eta_{rel.}$ or η_{sp}/c will suffice. But instead of these values, obtainable only with dilute solutions, we suggest that the critical velocity gradient $\hat{G}$, from the flow curve, be introduced as the molecular weight-dependent parameter. Since this value is independent of the concentration, the concentrated solutions used in industry may be used for the measurement just as they are, even if the concentration is not known.

Mention has already been made of the fact that both weight-average molecular weight and molecular weight distribution affect the shape of the flow curve. Since the ideal flow curve for a monomolecular high polymer is unknown, this

non-uniformity cannot be derived mathematically from the flow curve. Such a derivation became possible only after Umstätter[13] suggested a way of depicting the flow curve as a straight line. For the probability graph papers, No. 297 ½ A3 of Schleicher and Schüll, or No. 485 of the Schafer Verlag, Plauen/Vogtland, the abscissa has been divided logarithmically, and the ordinate according to the Gauss integral. If, in this graph, the values for

$$\frac{\ln \eta/\eta_\infty}{\ln \eta_0/\eta_\infty}$$

are plotted on the ordinate against the velocity gradient G belonging to each η', one obtains a flow curve appearing as a straight line. The flow curves for all concentrations of a macromolecular substance are represented by the same straight line. The critical velocity gradient $\hat{G}$, which depends upon the average molecular weight, can be read with great accuracy from the point at which the 50% line and the straightened flow curve intersect.

The slope of this straightened flow curve now provides a mathematical value for the polymolecularity of the dissolved macromolecular substance. The steeper the slope, the more uniform in molecular weight is the high polymer. At Umstätter's suggestion the straight portion between the 75% and 25% lines was projected on the abscissa. This length, in cm, was then divided by the abscissa unit in cm and expressed in decibels (db). In this way an absolute value is derived for the non-uniformity (U). A relative value for nonuniformity can be obtained by computing the variation coefficient as a relative value, via the standard deviation, which is an absolute value.

We will concede, of course, that when the molecular weights are substantially below 100,000 the region of η_∞ cannot yet be attained with the measurement techniques and equipment now available, and that there is indicated a certain amount of estimation in this region within the error limits. But it must be stated emphatically that in this case the estimation is justified, since all the solutions of macromolecular substances, for the reasons given, will always display symmetrical flow curves. This makes it possible to obtain, from the linearized flow curve, a value that is a function of the weight-average molecular weight, and, coincidentally, to derive a numerical value for the polymolecularity of rubber, and, naturally, of other macromolecular materials as well.

EXPERIMENTAL

Smoked sheets were used in the experiments because they represent a form of natural rubber that shows degradative effects more distinctly. Individual tests were made with stock masticated to varying degrees, since mastication not only leads to radical changes in viscosity and therewith in molecular weight, but is important in achieving the "softness" (Defo value) necessary for processibility. A number of factors are involved in this Defo value, and their accurate determination has been advanced to the realm of possibility by establishing the factors "molecular weight" and "polymolecularity". Analytical data for the smoked sheets used are presented in Table I.

The mechanical degradation of this rubber, i.e., mastication, took place on a laboratory mill under the following conditions:

Friction: 1.2
Roll nip: 1 mm
Rate passed through: 1200 cm/min

TABLE I

ANALYTICAL DATA FOR THE SMOKED SHEETS

	Test material	From the literature[14]
Moisture	0.6%	0.3–1.2%
Acetone extract	2.1%	2.5–3.2%
Protein	1.7%	2.5–3.5%
Ash	0.3%	0.15–0.5%
Rubber hydrocarbon (as difference)	95.3%	92.2*–94.0%

* The French and English editions of Reference 14 give 92.0 (Translator).

The number of passes through the rolls, corresponding to each stage of mastication, the temperatures attained and the Defo and plasticity values can be seen in Table II. The maximum temperature reached was 54° C, so there can be no question of thermal degradation. Due to the extensive breakdown, the material which was passed through the mill 200 and more times becomes increasingly tacky and viscid.

In the preparation of the test solutions we followed the proposals of Fol[15], whereby a representative test specimen of the rubber to be tested was cut into small pieces and thoroughly dried in a vacuum desiccator over concentrated

TABLE II

PROCESSING OF SMOKED SHEETS

No. of passes	Max. heat build-up during milling (° C)	Defo and plasticity value (av. of 10 measurements)
0	26	3300/39
10	31	3100/37
100	50	800/27
200	52	340/17
600	54	130/4
600 (cold)	35	55/3

sulfuric acid. Then followed weighing in a Jena brown-glass bottle, addition of the appropriate quantity of solvent and careful shaking every two hours. After standing for three days in the dark the solution was filtered through a glass frit (Schott G 1) to remove the insoluble portions.

Toluene seems to be a particularly appropriate solvent for obtaining the flow curves. The masticated test material is allowed to stand for about three days before being dissolved. Likewise, the filtered solutions are stored for three days before testing begins. Favorable concentrations for measurement at each mastication stage are given in Table III.

TABLE III

DEPENDENCE OF SELECTED CONCENTRATIONS ON THE NUMBER OF PASSES

No. of passes	Concentration
0	2 g/100 ml toluene
10	4 g/100 ml toluene
100	8 g/100 ml toluene
200	16 g/100 ml toluene
600	16 g/100 ml toluene

Since protein and ash are insoluble in toluene, rubber used in the investigation is essentially free of admixtures. We dispensed with the removal of the natural antioxidants and other stabilizers, because the methods required to do this would alter the molecular weight and thus not be conducive to improved results.

The rheological measurements were carried out with an Umstätter structure viscometer[16] having an accuracy of $\pm 1\%$. Details of the procedure for these measurements and their mathematical evaluations have already been supplied by Edelmann[17]. Figure 1 shows the flow curves for 2% and 4% solutions of unmilled smoked sheets in toluene by means of the new type diagram whereby the viscosity η' measured for each shear stress is plotted against the corresponding velocity gradient G in a log-log system of coordinates. The regions η_0 and η_∞ are located, like the viscosity of the Newtonian liquids, on straight lines

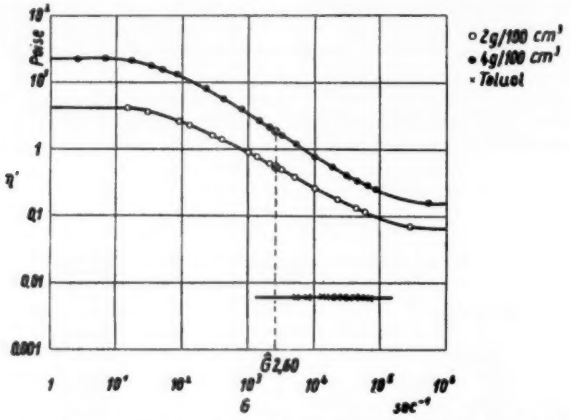

FIG. 1.—Flow curves of 2 and 4 per cent solutions of unmilled smoked sheets in toluene.

parallel to the abscissa, and the inflection point in each flow curve, corresponding to the critical velocity gradient $\hat{G}$, lies halfway between η_0 and η_∞. For both concentrations $\hat{G}$ has the same value, so that here, too, the lack of dependence of the concentration on the critical velocity gradient is clearly discernible.

This newer method of drawing the flow curve is an improvement over that of Philippoff[9] in that it shows directly the amount by which the measured viscosity η' will diminish in going from η_0 to η_∞, thus providing a direct indication of the viscosity range of the structurally viscous region. Through this method can be visualized the symmetry of all flow curves for solutions of chain macromolecules having a sort of Gaussian distribution. When these flow curves are transformed to straight lines, Figure 2, further corroboration is furnished of the rule that the flow curves of the various concentrations of a macromolecular material can be represented by a single straight line. The value for the critical velocity gradient $\hat{G}$ can be determined with great precision by the intersection of the linearized flow curve with the 50% ordinate. The slope of these straight lines provides a numerical value for the nonuniformity. Following the proposal of Umstätter, the portion of the linearized flow curve between the 25%

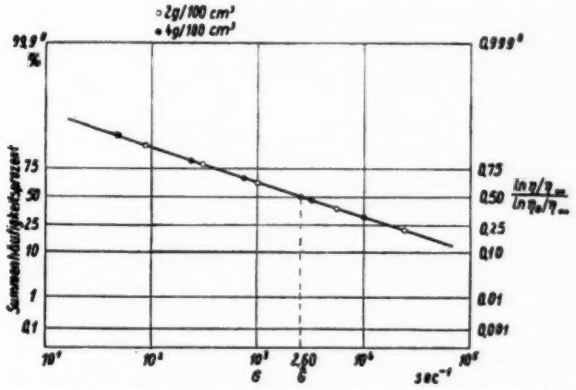

FIG. 2.—The linearized flow curves of 2 and 4 per cent solutions of unmilled smoked sheets in toluene. Ordinate: cumulative frequency, per cent.

and 75% ordinates is projected onto the abscissa and this value in cm is divided by the scale unit in cm and expressed in decibels (db). In this manner one obtains an absolute value for the nonuniformity. Another possibility for expressing, in this case, the polymolecularity by means of a numerical value, would to be establish the standard deviation as an absolute value and the variation coefficient as a relative value[8]. But then, the question of whether polymolecularity can be stated, for practical purposes, more advantageously in absolute or in relative values still requires careful discussion.

Figure 3 shows flow curves for smoked sheets during mastication, as represented by the new type of flow diagrams. In each case, after a certain number of passes through the mill, a test specimen is removed and the flow curve is plotted after dissolution in toluene. This is a clear demonstration of the rule that molecular weight and critical velocity gradient are inversely proportional

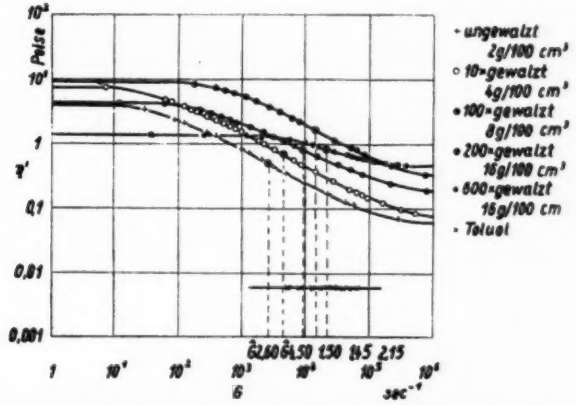

FIG. 3.—Flow curves of solutions with different concentrations of smoked sheets in toluene during mastication. Gewalzt = milled; ungewalzt = unmilled.

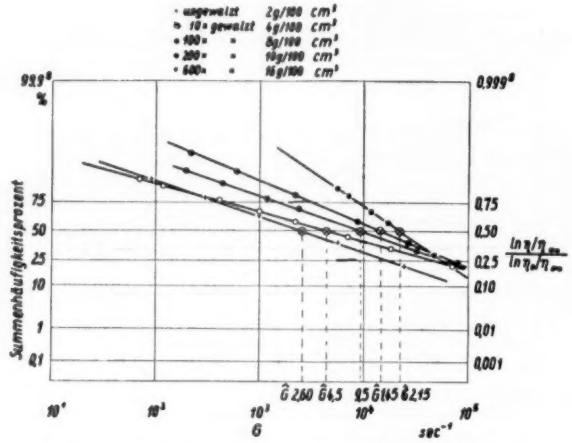

FIG. 4.—Linearized flow curves for solutions of smoked sheets in toluene during mastication. Ordinate: cumulative frequency, per cent.

since, as the number of passes increases, i.e., as the molecular weight is reduced, the critical velocity gradient takes on progressively higher values.

Since molecular weight diminishes strongly with the number of passes, it is recommended that concentrations be raised to compensate for the drop in molecular weight, so that curves will result which have a clearly delineated structural viscosity. On account of the independence of the viscosity on the concentration and the difference in polymolecularity, the individual flow curves intersect each other in this type of diagram. For this reason the representation proposed by Umstätter, viz. a linearized flow curve, is doubtless the best. The flow behavior of all the concentrations of a dissolved macromolecular substance in the same solvent is expressed by the same straight line.

Thus, in Figure 4, the flow curves of Figure 3 are presented as straight lines. Here it is quite plain that the molecular degradation progressing with the number of passes through the mill causes the critical velocity gradient $\hat{G}$ to

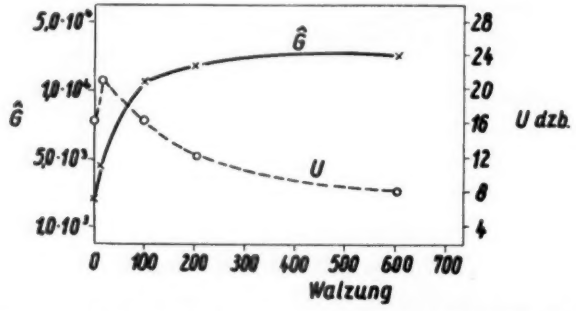

FIG. 5.—Degradation of smoked sheets due to mastication, represented as critical velocity gradient, $\hat{G}$, and polymolecularity, U. Dzb = decibels; abscissa: no. of passes through the mill.

TABLE IV

CHANGE IN MOLECULAR WEIGHT, CRITICAL VELOCITY GRADIENT AND POLYMOLECULARITY DURING MASTICATION

No. of passes	$M_{visc.}$	$\hat{G}$	U
0	$17.78 \cdot 10^5$	$2.6 \cdot 10^3$	16.50
10	$95.50 \cdot 10^4$	$4.5 \cdot 10^3$	21.20
100	$15.85 \cdot 10^4$	$9.5 \cdot 10^3$	16.40
200	$10.70 \cdot 10^4$	$1.45 \cdot 10^4$	13.22
600	$87.1 \cdot 10^3$	$2.15 \cdot 10^4$	8.34

shift continually to higher values so that the numerical values for $\hat{G}$ can be read off with great accuracy. Furthermore, the slopes of these straight lines furnish a numerical value for the polymolecularity. The greater the slope, the more homogeneous is the molecular weight distribution of the rubber. The linearized flow curve representing rubber milled ten times has a slope which is less steep than that for unmilled rubber. Due to the small number of passes only a few macromolecules are degraded, so that the nonhomogeneity is increased because of the supplementary scission products. But subsequently the straight lines get steeper with increased milling, i.e., as deterioration progresses the rubber becomes more homogeneous.

The results are portrayed in Figure 5, the molecular weight-dependent, critical velocity gradient $\hat{G}$ being plotted against the number of times the rubber was passed through the mill. In this graph, it is clearly seen that the molecular weight drops sharply at first, then diminishes more and more slowly, apparently approaching a limiting value. On the right ordinate the polymolecularity is simultaneously shown as a nonhomogeneity U in decibels, against the number of passes. In this way the rising inhomogeneity at the beginning of the milling is particularly noticeable, whereas the rubber becomes more homogeneous as its degradation continues.

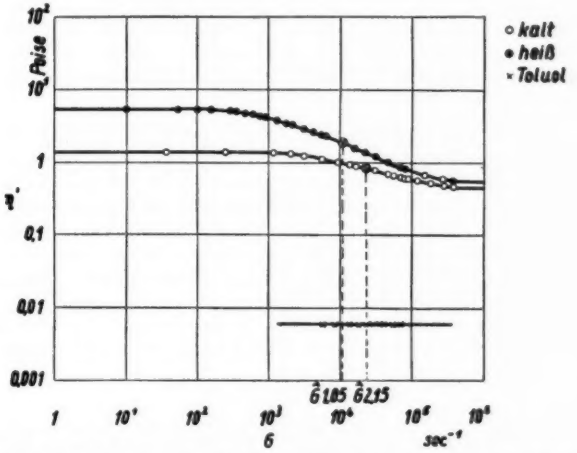

FIG. 6.—Flow curves for smoked sheets in toluene after 600 passes, hot and cold; o cold; • hot; x toluene.

In order to provide, in addition, incontrovertible proof that the critical velocity gradient is inversely proportional to the molecular weight, and hence represents a value dependent on the weight average molecular weight, we have compared, in Table IV, the molecular weights obtained by the relative viscometric method, with absolute viscometric values. The formula given by Carter and coworkers[18] was used for the relative method:

$$M_{visc.} = \sqrt[a]{\frac{[\eta]}{K}}$$

The constants valid for toluene are $K = 5.02 \cdot 10^{-4}$ and $a = 0.67$. It is plainly evident that as the molecular weight decreases with the number of passes through the mill the critical velocity gradient correspondingly increases. The numerical values for each polymolecularity are also tabulated.

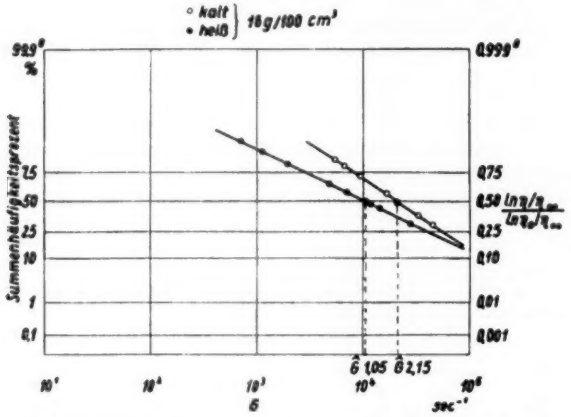

FIG. 7.—Linearized flow curves for smoked sheets in toluene after 600 passes hot and cold. Ordinate: as in Figures 2 and 4.

In this work we also investigated the well-known phenomenon that a cold-milled rubber is more severely broken down than a hot-milled rubber, in order to see how this affects flow behavior. Figure 6 shows the flow curves of 16% solutions in toluene of the same smoked sheets, after 600 passes through a cold mill and after 600 passes through a hot mill. In accord with the greater degradation of the cold milled rubber, the critical velocity gradient of its flow curve has a higher value than that of the hot milled rubber. The linearized flow curves of both solutions in Figure 7 once again give a clear demonstration of this effect. Further, the steeper slope of the straight line for cold milled rubber indicates greater uniformity as compared to hot milled rubber.

SUMMARY

Using the mastication of rubber as an example, it is shown how rheology can be utilized, even in the industrial processing of macromolecular substances, to obtain, from an easily and quickly determined flow curve, a value dependent

on the weight average molecular weight, and a numerical value for the polymolecularity.

Solutions of chain macromolecules with a sort of Gaussian molecular weight distribution give a symmetrical flow curve with an inflection point which, as the velocity gradient which is independent of the concentration, is a function of the average molecular weight. At the same time the slope of the linearized flow curve provides a numerical value for the polymolecularity of the material in question. In this way, even those changes in a macromolecular substance which occur during factory processing can be measured, as is the case here with masticated rubber.

ACKNOWLEDGMENT

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THE SIGNIFICANCE OF RHEOLOGY IN RUBBER PROCESSING. 2. STUDIES OF LATEX *

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INTRODUCTION

It was shown in the first communication[1] that solutions of chain-like macromolecules which have a sort of Gaussian molecular weight distribution, such as smoked sheet, show a symmetrical flow curve with a point of inflection at a critical velocity gradient which is independent of concentration, but is dependent upon the weight average molecular weight. Furthermore, the slope of the linearized flow curve provides a numerical value for the polymolecularity of the particular macromolecular substance.

The rubber molecules in a solution are dispersed as deformable coils between the solvent molecules, but in latex the rubber is subdivided in the form of liquid droplets dispersed in water. This differently constituted colloid system should lead to a different flow behavior, as will be described in this work. Originally, the word "latex" meant simply a water emulsion of natural rubber. Today the word has a much broader interpretation since it includes all the water emulsions of synthetic latex compounds and their additives. These additives are also, in part, macromolecular substances and, in part, electrolytes, which can greatly change the flow characteristics.

The technical use of latex offers the advantage that in the processing there is avoided chain scission by mastication which must be reversed to some extent by chain coupling during the connective vulcanization.

For this reason, latex is being used in ever increasing amounts, instead of rubber solutions, in the manufacture of articles by dipping processes, in the production of threads by extrusion into a coagulant, for impregnation of textiles, etc.

With the increasing use of latex, it becomes more and more urgent to devise new methods of studying this colloidal system, so that reproducible characterization of a particular latex may be assured. In this second communication it will be shown how likewise in the latex processing industry, from rheological measurements worthwhile conclusions can be drawn about the condition and quality of a latex. Thus, from a knowledge of its flow characteristics, a latex with the necessary flow behavior can be chosen for some special mechanical processing, such as the production of foamed rubber, adhesives, and latex paints.

THEORY

The flow behavior of the latex system can be explained from the colloidal properties. Pure latex is a liquid-in-liquid colloidal dispersion, that is, an emulsion. It can also be designated as an oil hydrosol. The two immiscible liquids are the elastomer which constitutes the dispersed phase in the form of

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe, from *Gummi and Asbest*, Vol. 12, pages 66, 68, 70, 72, 74, 75, February 1959.

droplets of about the same size, and water as the dispersion medium. Especially in the case of synthetic latexes, a variety of emulsifying and stabilizing materials are present on the boundary surfaces of the dispersed phase. The nature of these surfaces and changes which occur at them determine the rheological properties and the stability of a latex system.

In order that an emulsifier may be effective, it must be able to form a film which to a degree is absorbed on the dispersed droplets. The stability of the emulsion depends upon the nature of this film. If a reaction takes place between the emulsifier and an electrolyte, the electrical charge will exert a strong influence on the stability of the whole system. Thus we get a clear idea of the colloidal state of a latex. According to McBain[2], the surfaces in such colloidal systems exert an influence which is effective over much more than a monomolecular thickness. Such forces, similar to Van der Waals forces, must be thought of as explaining the formation of structures such as appear to be present in thixotropic or pseudo-plastic latex systems.

The stability of a colloidal system depends much upon the elimination of irreversible changes and coagulation. Materials are often added to a latex system to improve its stability which cause a thickening or creaming or other reversible rheological changes. The thickening is also associated with a growth in particle size. The stability of a latex must be ascribed to the electric charge at the interfaces and to the degree of hydration, or amount of bound water.

The time factor is of great importance in the stability of the latex system for stability changes with time as do the rheological properties. In general, the synthetic latexes have a smaller particle size than is found in natural latex. As a result the surface area is much greater and they require a larger amount of stabilizer in order to attain the same effects. Comprehensively it may be said that the rheological behavior of a latex system is affected by:

1. Absorbed mechanical films
2. Electrical charges
3. Van der Waals forces
4. Degree of hydration
5. Loose structure

Thickening agents which are usually added, such as cellulose derivatives[3], bentonite[4], polyvinyl alcohol or acetate[5] and sodium polyacrylate[6] are decidedly hydrophilic colloids, and their water solutions show pronounced deviations from Newtonian flow. The pronounced thixotropy of water dispersions of sodium bentonite is especially well known[7]. If such thixotropic systems are added to a latex as thickeners, they modify the flow characteristics of the respective latex system[8,9], since they build up weak chain structures. Stable latexes with controllable rheological characteristics may be made in this way[10]. The rheological behavior of a latex cannot be predicted from a knowledge of the colloidal properties of the dispersion of the thickening agent alone.

In pure latex, the disperse phase consists of semi-solid spheres, representing the smallest surface area[11]. At an adequate dilution these tiny spheres will scarcely vary in form when subjected to a shearing stress. Hence Newtonian flow behavior is to be expected in the case of a diluted pure latex, just as is found in the case of the spherical macromolecules of egg albumin. On the other hand, more concentrated latex systems are to be thought of as complex, pseudoplastic fluids. Hence Krieger and Maron[12] have proposed an exponential flow equation for the entire shear stress range for latexes ranging from 25 to

45% concentration. While retaining the equation for calculating values of shear stress P in the capillary viscometer,

$$P = \frac{Rp}{2L}$$

where R = radius of capillary, p = applied pressure, L = capillary length, they introduce a correction factor, N, in the equation used for calculating the velocity gradient, G, for Newtonian flow:

$$G = \frac{4Q}{\pi R^3 t}$$

where Q = amount discharged, t = time, so that this equation then reads

$$G = \frac{(N+3)Q}{\pi R^3 t}$$

This kind of exponential flow curve has been already used by Porter and Rao[13] as well as by Jarrow, Lowe and Neale[14] in analogous cases, since they correct the shear stress P with an exponent N in calculations of viscosity η'. The flow equation for this non-Newtonian flow behavior then reads:

$$\eta' = \frac{P^N}{G}$$

For latexes above 45% concentration, Krieger and Maron[12] had to use different correction factors for both the lower range and the higher range of shear stress. Thus it is not possible to define the flow behavior of a concentrated latex over the whole range of shear stress with one single flow equation. Yet these authors could not establish the presence of thixotropy in pure latexes. It is only when latexes are treated to stabilize them with thickening agents and electrolytes, that the characteristics of thixotropy appear.

Thixotropy, which we encounter here, is one of the most disagreeable of the anomalous flow characteristics. It is a reversible gel-sol condition and comes about through the self-forming, weak structure in the liquid. According to Mooney[15], a thixotropic system owes its existence to aggregates of dispersed particles. Only after a period of rest can these aggregates reform, so the restoration relations are dependent upon previous shear stresses. Thixotropy is noted especially in systems containing a large quantity of bound water, so the degree of hydration must exert an influence.

The fundamental work on thixotropy was reported by Freundlich[16] and Winkler[17]. According to them, thixotropy is evident in those colloidal systems in which rather large amounts of dispersing agent are absorbed by the particles, so that finally the particles show no more Brownian movement and chains or feeble networks are formed by the packed particles. Thus the immobilized particles can be held by far reaching electrical forces or by thick solvate layers.

The appearance of thixotropy must therefore be considered as a complex phenomenon, because it depends not only on the composition of the specific system, but also on other factors, especially time and the magnitude of the shear stresses. It will therefore be dependent upon the dimensions of the apparatus used in testing. As a result of these facts there is no definition for the degree of thixotropy. There are given only suggestions for a relative value,

a so-called "Index of Thixotropy", as a quotient of or difference between two readings on a rotary viscometer[10]. In addition, special instruments to use in the study of thixotropy have been devised by Pryce-Jones[18].

EXPERIMENTAL

The experiments which were carried out showed that the flow behavior of latexes could be measured over a wide range of shear-stress with a Höppler Rheo-viscometer. This apparatus has an advantage over narrow capillaries in the ease of cleaning the adhering film from the container. A disadvantage, of course, lies in the fact that the streaming around the sinking body cannot be mathematically calculated, so the velocity gradient can be calculated only indirectly from the Newtonian start of the viscosity. The Höppler-Consistom-

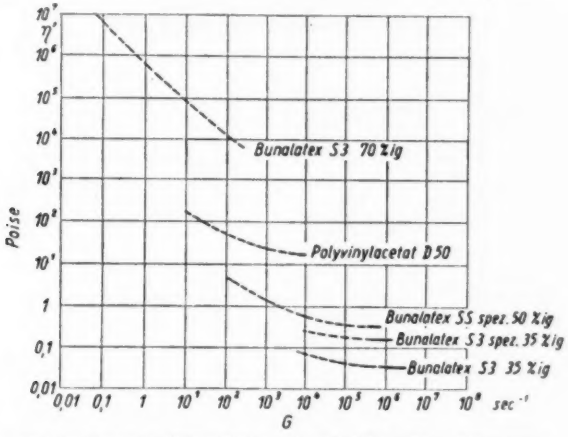

FIG. 1.—Curves for different latexes shown by the new type of flow curve.

eter had to be used only with the 70% Buna-Latex because the range of the Rheo-viscometer was not wide enough for such high viscosities. All measurements were made at 20° ± 0.01° C.

In Figure 1 are given the flow curves for the various latex systems which were studied, using the same coordinates, η' against G, which were used for rubber solutions in the first communication[1]. The fundamentally different flow behavior is apparent. The region of η_0, the viscosity at rest, is absent. The symmetry of the flow curves is also lacking. The curves given here show merely a drop in the viscosity with increasing velocity gradient, as for non-Newtonian liquids, until the non-Newtonian goes over into the Newtonian flow pattern at a certain value of the velocity gradient. The non-Newtonian flow range is shown in Figure 1 by broken lines for the individual latexes, while the Newtonian range is shown by solid straight lines parallel to the abscissa. The region of Newtonian flow could not be reached by the Höppler-Consistometer in the case of the 70% Buna-Latex S3.

If we follow the curves toward the lower velocity gradients, a "fluid limit" is indicated at which the latex first starts to flow. This critical value is outside of the range of measurements. Then follows the region of non-Newtonian flow

where the loose aggregates of dispersed particles are more and more destroyed with rising velocity gradient, until, at a high velocity gradient, specific for each case, the aggregates are so completely disrupted that the latex system follows the Newtonian definition of viscosity. Thus the non-Newtonian range of flow behavior can be thought of as a "preliminary process" which naturally depends on the immediate "past history" of the sample, that is on how strongly the system being measured has been agitated before the measurement is made. From this rheological behavior it is apparent that the latex system shows "thixotropy".

The "hysteresis loop" method is used here to show the thixotropy of the individual systems which were studied. In this method the viscosity of the system is measured through a range of increasing shear stresses and then

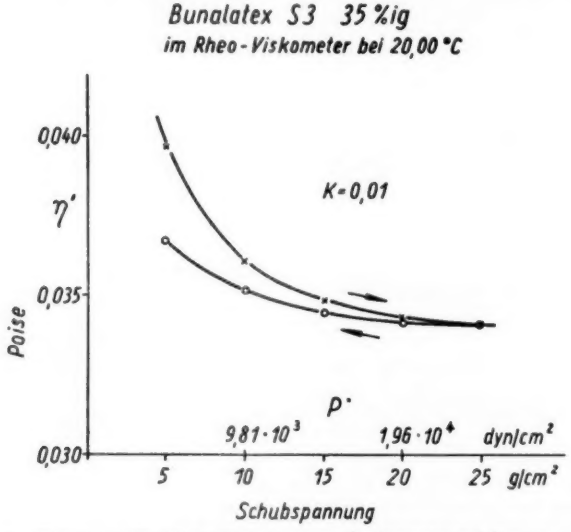

FIG. 2.—Rheogram of Buna-Latex S3, 35%, measured at increasing and decreasing shear stresses. Ordinate: Poises; Abscissa: Shear stress.

through a corresponding range of decreasing shear stresses. In this way the following "rheograms" were derived. Since the velocity gradient is calculated indirectly for measurements with the Höppler Rheo-viscometer, but the applied shear stress is known accurately, the measured viscosity η', in poises, is here plotted against the applied shear stress in g/cm². For comparison the shear stress is also given in absolute units, dynes/cm², in Figure 2. Since thixotropy is a complex value because of its dependence on other factors such as time and apparatus dimensions, this conversion can be dispensed with.

In Figure 2 is given the hysteresis loop for a 35% Buna-Latex S3 tested in the Höppler Rheo-viscometer with measuring container $K = 0.01$. The viscosity η' as measured at increasing shear stresses decreases until it reaches a constant value at a definite high shear. From this point on, with increasing shear stress, the flow behavior is Newtonian, and this is shown in this coordinate system by a straight line parallel to the abscissa. If the measurements are made

with decreasing shear stresses the viscosity values do not lie on the same curve. As in the case of solutions of macromolecules in solvents, the viscosities are lower than the values obtained in the measurements with increasing shear stress. The original value of the viscosity will be reached again only after a certain period of rest, and thus the hysteresis loop will be closed. This flow behavior is clear proof of the presence of thixotropy. With increasing shear stress the loose aggregates are progressively disintegrated until finally the sol stage is reached and the latex shows Newtonian flow. On the other hand, in the case of decreasing shear stress, the aggregates cannot build up so rapidly and consequently lower viscosity values are shown. In this way, it is clearly seen how the time dependence of the viscosity is a question of the "past history", or the stresses which have just been applied to the system.

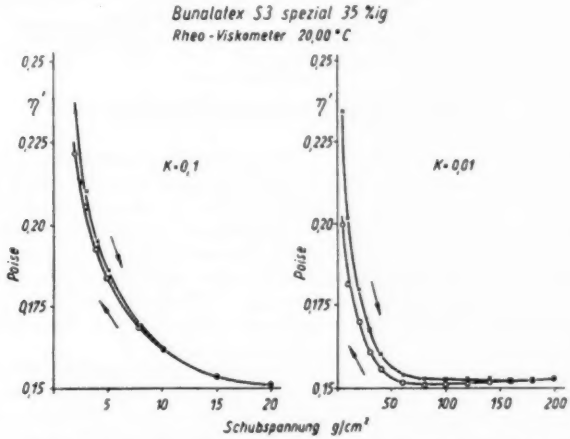

FIG. 3.—Rheogram of Buna-Latex S3 special, 35%, measured in different measuring containers. Coordinates as in Figure 2.

In order to show the dependence of thixotropy on the apparatus, the hysteresis loops for a 35% Buna-Latex S3, measured under identical conditions but with two measuring containers, $K = 0.1$, and $K = 0.01$, are given in Figure 3. As a result of the larger shearing stresses in the narrower container $K = 0.01$, it can be seen that the differences between viscosities measured at increasing and at decreasing shear stress are greater than those when the wider container $K = 0.1$ was used. Moreover it can be seen that in the case of the narrower container, $K = 0.01$, there is a further decrease in the viscosity when decreasing shear stress is used. This results from the preceding shear stressing. In this case there must be additional disruption of the aggregates, and they can only begin to reform at somewhat lower shear stresses. This is shown by the increasing viscosities at still lower shear stress. This behavior also illustrates the time dependence of viscosity on the "prehistory", an evidence of thixotropy.

A concentrated 50% Buna-Latex SS also shows great differences in the hysteresis loops for measurements with the two containers $K = 0.1$ and $K = 0.01$. This is shown in Figure 4. Whereas Newtonian flow starts with the $K = 0.1$ container at a shear stress of about 10 g/cm² and a viscosity of 0.41

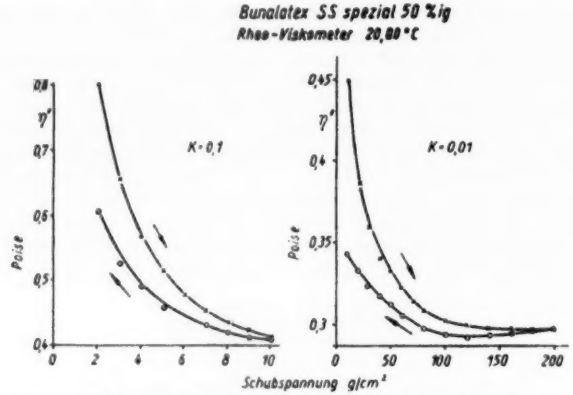

FIG. 4.—Rheogram of Buna-Latex SS special, 50%, measured in different measuring containers. Coordinates as in Figure 2.

poise, Newtonian behavior starts at a shear stress of about 100 g/cm² and a viscosity of 0.30 poise when the $K = 0.01$ container is used. This difference in Newtonian viscosity can be explained simply by the additional destruction of the aggregates when the narrower container is used. But even at this Newtonian flow, all the aggregates are not broken up, for the following measurements made with decreasing shear stresses show decreases in the viscosity resulting from the preceding vigorous shearing. This occurs before the rebuilding of the aggregates at smaller shear stresses is perceptible by an increase in the measured viscosity.

Polyvinyl acetate D50 was studied as a typical thickening agent in this same way. Its thixotropic behavior is shown in Figure 5. Because of the higher viscosity, the wider measuring containers $K = 100$ and $K = 1$ were used. The hysteresis loops show the extraordinarily strong thixotropy of these preparations.

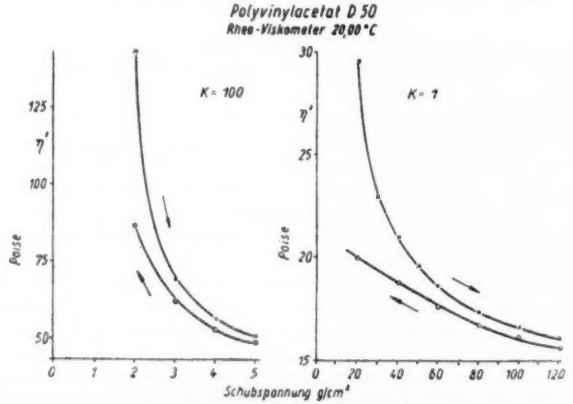

FIG. 5.—Rheogram of polyvinyl acetate D 50 measured in different measuring containers. Coordinates as in Figure 2.

The viscosity measured in the container $K = 100$ is 143 poises at 2 g/cm² shear but it falls to 16 poises at a shear stress of 120 g/cm² when measured in $K = 1$, and the region of Newtonian flow is still beyond the measuring limits of the apparatus. Even so, the rebuilding of the aggregates takes place slowly, as is shown by the gradual rise in the viscosity when measured at decreasing shear stresses.

Finally, the thixotropic behavior of a 70% Buna-Latex S3 is shown in Figure 6. Because of the high viscosity, the shear stress range of the Rheoviscometer was not wide enough to span the measurements of this system. Hence the Höppler-Consistometer was used. The measurements show a very different thixotropic behavior by this concentrated latex as compared with that of the other latexes which were studied. Thus, the curve obtained with increasing shear stresses lies below that for the viscosities obtained with decreas-

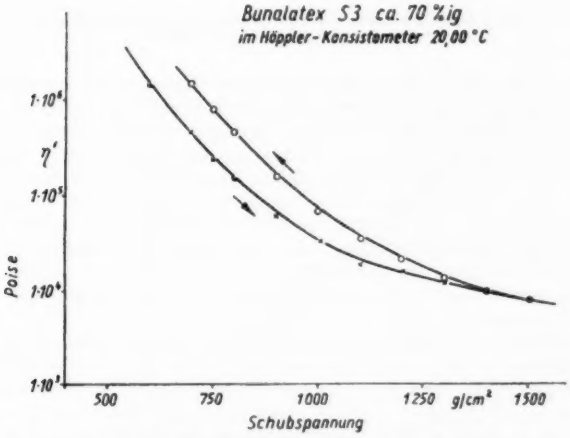

FIG. 6.—Rheogram of Buna-Latex S3, about 50%, measured in the Höppler-Consistometer. Coordinates as in Figure 2.

ing shear stresses. This is the reverse of the relative position of these curves for all the other latexes which we have studied. This different sort of thixotropic flow behavior may be explained by the fact that this latex does not consist of a fluid with weak aggregates of dispersed particles, but it is a gel with a well built-up three dimensional structure throughout. Under the force of the relatively high shear stress the gel breaks at various places and the viscosity sinks relatively rapidly. But in the case of decreasing shear stresses there is less breaking up of the structure because of its higher gel strength, and higher viscosity values are measured. This phenomenon has previously been noted by Leaman[10]. Furthermore it is not possible here to reach the range of Newtonian flow, because of the limitations of the apparatus. Yet the viscosities measured at the highest attainable shear stresses are identical for the increasing and decreasing shears. It is possible that such high viscosity measurements are so insensitive that small differences can not be detected.

In summary, it can be said that a rheological study of latexes, that is to say a study over a range of shear stresses and shear rates, will tell much more than a

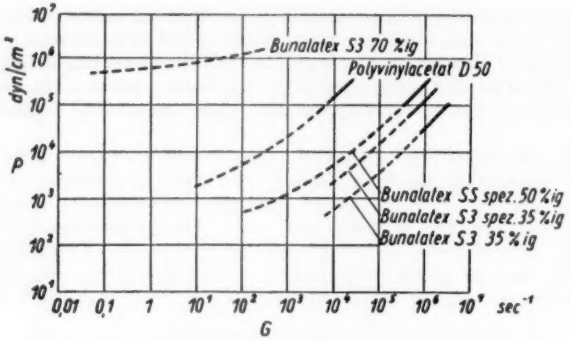

FIG. 7.—The flow curves of Figure 1 drawn as shear stress (ordinate) against velocity gradient (abscissa).

single test of viscosity. Either the latexes are characterized according to their thixotropy, or the range for Newtonian flow is sought for under the given experimental conditions in order to arrive at more accurate values.

An exponential flow equation for latexes has been given by Krieger and Maron[12], which is applicable when capillary viscometers or rotating viscometers are used. Since the Höppler Rheo-viscometer is convenient to use and relatively easy to clean, but the flow around the falling body in this apparatus cannot be mathematically defined, an exponential flow equation for this apparatus is derived from the deviations from Newtonian flow, which applies to all latexes which show Newtonian flow behavior in the range where measurements can be made.

The viscosity η is defined according to Newton as the quotient of the shear stress P divided by the velocity gradient G. Hence the behavior of the latexes is again shown in the log-log plot, P against G, in Figure 7. Here a Newtonian behavior is shown at higher values of shear stress and shear rate by the straight lines with slope of 45°. With the exception of the 70% Buna-Latex S3 all the latexes reach into this Newtonian range as is shown by the solid sections of the lines, while the deviating ranges are shown by broken lines.

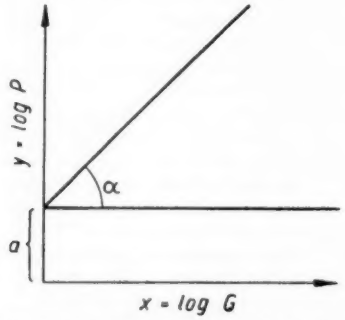

FIG. 8.—Position of the line for Newtonian flow in the graph, log shear stress against log velocity gradient.

In general, Newtonian flow behavior can be shown as straight lines with 45° slope when $\log P = y$ is plotted against $\log G = x$, as is done in Figure 8. The equation for the line then becomes:

$$y = a + bx$$

where

$$a = \log \eta \quad \text{and} \quad b = \tan \alpha \tag{1}$$

Also: $\log P = a + b \log G$ or $\log P = \log \eta + b \log G$ and hence

$$P = \eta G^b \tag{2}$$

which is the exponential function.

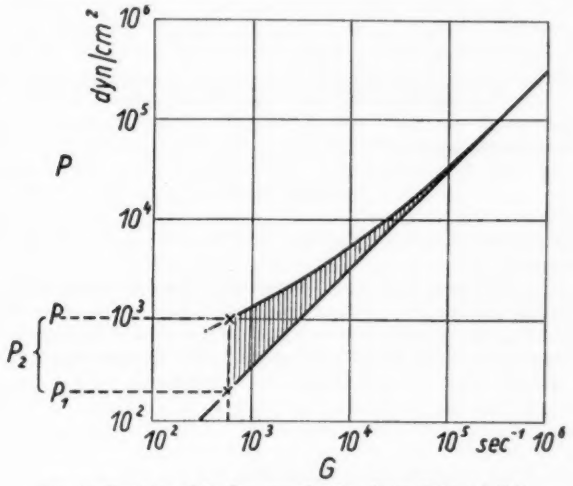

FIG. 9.—Deviation of the flow curve for Buna-Latex SS special, 50%, from the line for Newtonian flow.

In the special case of Newtonian flow, $b = \tan \alpha = 1$ and we have the Newtonian definition of viscosity:

$$P = \eta G$$

This Newtonian flow is reached in the case of the latexes studied, only at relatively high values of shear rate. For any chosen value of shear rate then, the shear stress is made up of the shear stress for Newtonian flow P_1 and a shear stress correction P_2, as shown in Figure 9.

In other words:

$$P = P_1 + P_2 \tag{3}$$

Analogous to Equation (2), we have:

$$P_2 = cG^d \tag{4}$$

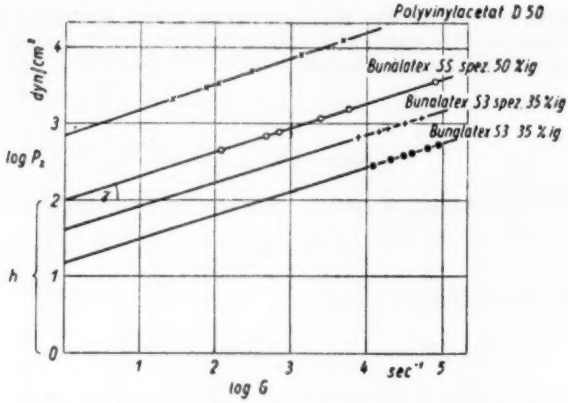

FIG. 10.—The position of the shear stress correction for different latexes in the graph of shear stress against velocity gradient.

and thus the complete equation for P is:

$$P = \eta G^b + cG^d \tag{5}$$

which is the general equation of flow for latexes, and which is applicable to the Rheo-viscometer.

For the Newtonian part, $b = 1$, so that only the constants c and d need be determined for each latex. For the determination of these constants, the logarithms of P_2, derived as in Figure 9, are plotted against the logarithms of the corresponding values of G, as shown in Figure 10. In this way a straight line is drawn for each latex, and the slope of the line is:

$$\tan \gamma = d$$

and its point of intersection with the ordinate is:

$$h = \log c$$

In this way the constants c and d in Equation 5 are evaluated.

Table I gives the calculated constants for the different latexes whose Newtonian flow behavior lies within the range of measurements. In these cases, the rheological relations can be defined by the general flow equation given previously. A different equation is necessary only for the gel-like latexes.

TABLE I

CONSTANTS FOR THE GENERAL FLOW EQUATION FOR THE LATEXES STUDIED

System studied	c	d
Buna-Latex S3, 35%	14.69	0.31
Buna-Latex S3 Special, 35%	39.41	0.31
Buna-Latex SS Special, 50%	100.0	0.31
Polyvinyl acetate, D 50	676.1	0.34

As has been mentioned, thixotropy represents, among other things, a quantity which varies with time. Since we had no exact data on the preparation of the latexes, the measurements which were made do not warrant drawing any further conclusions. No further statements can be made within the scope of this work about the physical significance of the constants which are used in the flow equation which is given. It may be possible by further studies of latexes with identical "past histories", to shed more light on this subject, and to explain more exactly differences in rheological behavior in dependence on the composition.

SUMMARY

After referring to the importance of rheological studies for the ever growing applications of latex in industry, results are reported for the study of the rheological behavior of several Buna latexes, using a Höppler Rheo-viscometer. The flow curves obtained in this way show a different type of non-Newtonian flow from solutions of rubber. The region of η_0, viscosity at rest, is absent. With increasing velocity gratient, the viscosity becomes smaller and smaller and finally reaches a constant value at a relatively high velocity gradient. That is, non-Newtonian flow passes gradually over into Newtonian flow.

For those latexes whose Newtonian flow lies within the measurable range, a general flow equation is given which includes the Newtonian portion of the shear stress together with a stress correction. This equation of flow can be used to define the rheological behavior of the latexes.

The cause of this type of rheological behavior is found in the thixotropic properties of the latex system. If a Höppler Rheo-viscometer is used and measurements are made first at increasing and then at decreasing shear stresses, the plotted data show a hysteresis loop which is evidence of thixotropy. With those latex systems for which the Newtonian flow behavior falls within the limits of the measurements, and which can be called fluids, the viscosities measured with decreasing shear stresses lie below those which are measured with increasing shear stresses.

On the other hand, highly concentrated latexes which can be considered as having a gel structure throughout, such as the 70% Buna-Latex S3 used in this work, display a different kind of thixotropic behavior. In such cases, the viscosities measured with decreasing stresses are higher than those measured with increasing shear stresses. A different flow equation is needed to define this different type of thixotropy.

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THE REACTION OF OZONE WITH SBR RUBBERS *

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It is well known that the action of ozone on styrene-butadiene rubber (SBR) vulcanizates that are under stress, either static or dynamic, causes a cracking of the surface[1-4]. This phenomenon takes place very readily on the surface of vulcanized SBR rubber, but the effect is both greatly delayed and reduced when various antiozonants, such as certain N,N′-di-alkyl-*p*-phenylenediamines or similar compounds, are incorporated in the rubber[5]. If a wax is also added in small quantities along with the antiozonant, the retardation of the attack of ozone on such rubbers is in certain instances enhanced several fold.

In order to study the action of ozone on SBR polymers, on SBR vulcanizates, on antiozonants, and on compounds that are used in rubber vulcanizates, it was considered important to know the rate of ozone absorption and the total quantity of ozone absorbed per mole of the substance with which the ozone reacted. The present paper deals with the method and procedures which were designed to obtain data which would reveal some of the kinetics of the reaction of ozone with SBR vulcanizates. The effect of additives, such as antiozonants, oil extenders and plasticizers, was also studied.

APPARATUS AND PROCEDURE

A modified form of the apparatus of Crabtree and Kemp was constructed as partially shown in Figure 1. The specimen to be studied was placed in the reaction chamber, *A*, in a manner depending on the nature of the specimen. In the case of the rubber vulcanizates, the specimen, in the form of a rod, was placed in a coaxial position with a clearance of 1 to 2 mm between the rod and the walls of chamber *A*. A static stress (20 per cent elongation) was applied to the rod by stretching the rod the calculated amount and securely fastening the upper clamp. A dynamic stress could be applied on the stressed rod by means of the ground glass sleeve and piston, *B*, at the lower end of the reaction chamber. The piston was connected to an eccentric drive, powered by a small motor. By means of a stopcock, *C*, the ozone-air stream could be directed either around the rod or through the by-pass for a blank determination.

In the case of a pure antiozonant, unvulcanized rubber, or other compounds, the specimen was deposited from an inert solvent on silica gel (60 to 80 mesh) in a column by the chromatographic method. The column, together with a blank, was then substituted in place of the reaction chamber.

In the work on the structural analysis of certain antiozonants for SBR polymers the specimen was placed in an inert solvent in a vessel which was substituted in place of the reaction chamber. The exit ozone air stream flowed

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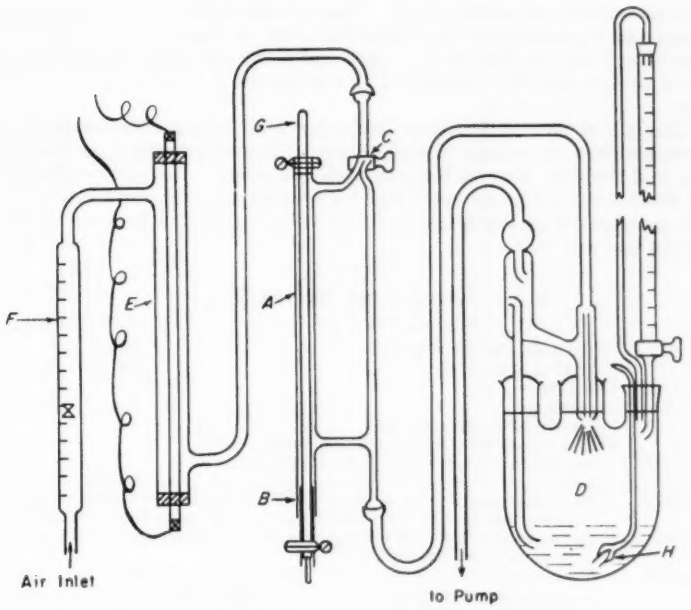


A Reaction chamber
B Sleeve and piston
C Stopcock
D Analyzer
E Ozone Generator
F Flowrator
G Rubber rod
H Platinum Electrodes.

FIG. 1.—Apparatus for determination of ozone absorption.

directly into the ozone analyzer through a spray-jet, where the ozone was removed in the conventional method by a buffered potassium iodide solution, and the iodine liberated was titrated intermittently by the addition of standard sodium thiosulfate. The ozone generator *E* was a quartz-mercury vapor lamp wrapped with aluminum foil, leaving an exposed length only sufficient to give

TABLE I

FORMULATION OF RUBBER RODS[a]—SERIES S12

	S12	S12B	S12B46	S12B68
SBR 1505 (90/10 at 41° F)	100	100	100	100
MAF[b] carbon black	50	50	50	50
Zinc oxide	3	3	3	3
Stearic acid	2	2	2	2
N-cyclohexyl-2-benzothiazolyl sulfenamide	1	1	1	1
Sulfur	1.75	1.75	1.75	1.75
N-phenyl-2-naphthylamine	1	1	1	1
Polymerized trimethyl dihydroquinoline	1	1	1	1
N,N′-di-*sec*-butyl-*p*-phenylenediamine	—	2	—	—
Wax	—	—	—	1
N,N′-di-*sec*-butylbenzidine	—	—	5.4	5.4

[a] Rods are 15 in. in length with a diameter of $\frac{3}{16}$ in.
[b] Medium abrasion furnace.

the concentration of ozone desired. The concentration of the ozone in the air stream and the strength of the thiosulfate were adjusted to give an end point every 3 to 5 min for the blank. Each end point was timed alternately by a pair of electric stop timers, operated by a microswitch, to obtain a record of the time.

The rate of flow of the ozone (moles per min) through the apparatus was calculated from the volume of each portion of thiosulfate added, its concentration, and the time interval between each end point. The rate of absorption and the quantity of ozone absorbed by a specimen at each end point in a run, were calculated from the difference in the rate of ozone flow between the blank and the test run.

TABLE II

FORMULAS FOR S64 AND S47[a]

Base compound	Parts
SBR 1500 (80/20 at 41° F)	100
MAF[b] carbon black	50
Zinc oxide	3
Stearic acid	2
N-phenyl-2-naphthylamine	1
Polymerized trimethyl dihydroquinoline	1
N-cyclohexyl-2-benzothiazolyl sulfenamide	1
Sulfur	1.75

S64B	Base compound plus 3 parts of N,N′-bis(1-ethyl-3-methylpentyl)-*p*-phenylene-diamine and 1 part wax per 100 parts rubber hydrocarbon.
S46E	Base compound plus 20 parts of trioctyl phosphate and 1 part wax per 100 parts rubber hydrocarbon.
S64BE	Base compound plus 20 parts of trioctyl phosphate plus 3 parts of N,N′-bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine and 1 part wax per 100 parts rubber hydrocarbon.
S64D	Base compound plus 37.5 parts of naphthenic processing oil and 1 part wax per 100 parts rubber hydrocarbon.
S64DB	Base compound plus 37.5 parts of naphthenic processing oil plus 3 parts of N,N′-bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine and 1 part wax per 100 parts rubber hydrocarbon.
S54DA	Base compound plus 37.5 parts of naphthenic processing oil and 1 part wax per 100 parts rubber hydrocarbon; N,N′-bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine was introduced into the rubber by dip-coating five times from a 50 per cent solution of the antiozonant in acetone.
S64B54	Base compound plus 3 parts of 1-(*p*-*sec*-butylaminophenyl)-2,5-dimethyl pyrrole and 1 part wax per 100 parts rubber hydrocarbon.
S65B54E	Base compound plus 20 parts of trioctyl phosphate and 3 parts of 1-(*p*-*sec*-butylaminophenyl)-2,5-dimethyl pyrrole and 1 part wax per 100 parts rubber hydrocarbon.
S64E1	Base compound plus 20 parts of naphthenic processing oil and 1 part wax per 100 rubber hydrocarbon.
S64B54E1	Base compound plus 20 parts naphthenic processing oil and 3 parts 1-(*p*-*sec*-butylaminophenyl)-2,5-dimethyl pyrrole and 1 part wax per 100 parts rubber hydrocarbon.
S64ED	Base compound plus 20 parts of trioctyl phosphate and 1 part wax per 100 parts of the rubber hydrocarbon. N,N′-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine was introduced into the rubber by dipcoating 5 times from a 50 per cent solution of the antiozonant in acetone.
S47	Base compound.
S47A3	Base compound plus 1 part wax per 100 parts rubber hydrocarbon.
S47B	Base compound plus 3 parts N,N′-bis(1-isobutyl-3-methylbutyl)-*p*-phenylenediamine per 100 parts rubber hydrocarbon.
S47A3B7	Base compound plus 1 part wax and 3 parts N,N′-bis(1-isobutyl-3-methylbutyl)-*p*-phenylenediamine per 100 parts rubber hydrocarbon.

[a] Rubber rods, 15 in. long, and $\frac{1}{4}$ in. diameter.
[b] Medium abrasion furnace.

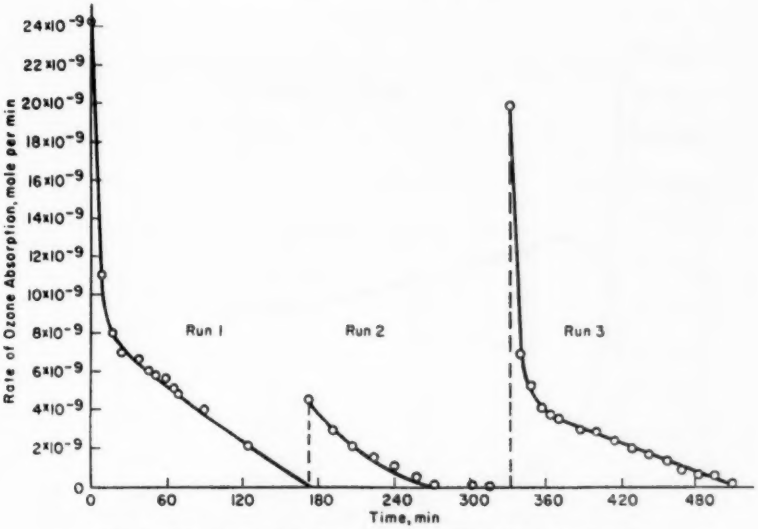


FIG. 2.—Rate of ozone absorption versus time, SBR rod S12, not under stress. Ozone flow rate, 2.5×10^{-8} mole per min.

All specimens of the vulcanizates were prepared in form of rubber rods by the Rubber Laboratory of the Rock Island Arsenal. The formulations are given in Tables I and II.

EXPERIMENTAL RESULTS

Relaxed state.—SBR vulcanizates, containing no antiozonant and under no stress, began absorbing ozone from an ozone atmosphere, ranging from 25 to 250 pphm (parts per hundred million) of ozone, with a high initial rate, but the rate declined rapidly with time until no further absorption could be detected. This phenomenon is shown in Figure 2 for vulcanizate S12. The rod was kept in the relaxed state for several hours between the first and second run. Before beginning run 3, the rod was subjected to a dynamic stress for a few minutes to break the surface film of oxidized products on the rubber surface. No ozone cracking was found under 32× magnification, but the initial glossy appearance of the surface had changed to a dull gray.

Static stress (20 per cent elongation).—In the case of SBR vulcanizates containing no antiozonants or wax, such as specimens S12 and S47, the curves of the rate of absoprtion versus time are similar to Figure 3. The rate of absorption of ozone began with initial value of zero but increased rapidly to a maximum which was followed by a slow decline. Ozone cracks appeared over the entire surface immediately before the maximum rate. The cracks appeared to relieve local stresses in the surface of the rubber, which caused a decline in the rate of absorption following the maximum value. The vulcanizate, S47A3, which contained 1 part wax but no antiozonant, gave similar results except that there were distinct indications that some ozone-sensitive material had migrated to the surface of the rubber. Although ozone cracks appeared on the rubber surface

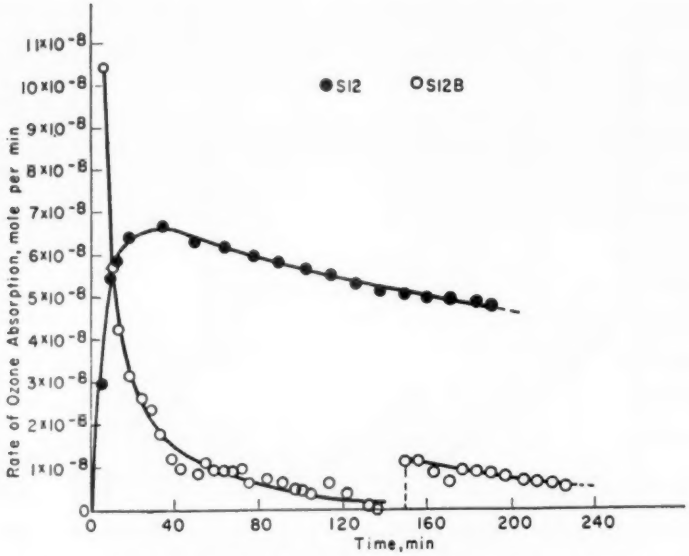


FIG. 3.—Rate of ozone absorption versus time, specimens under 20 per cent elongation. Ozone flow rate, 1.05×10^{-7} mole per min.

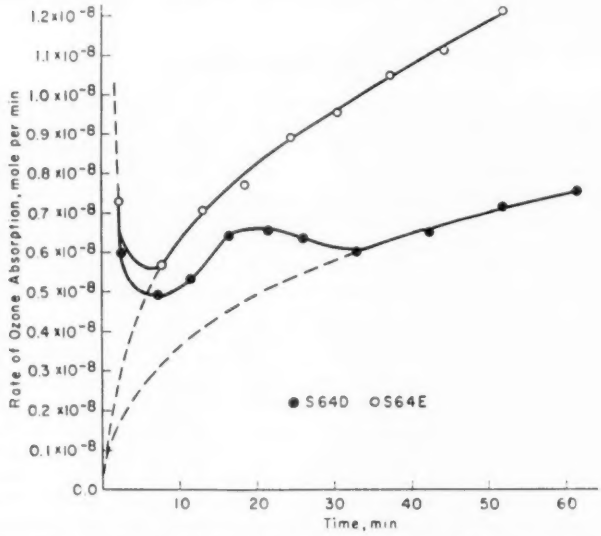


FIG. 4.—Rate of ozone absorption by rubber rods S64D and S64E under 20 per cent elongation.

TABLE III

DATA ON OZONIZATION OF SBR ROD, S12B68, CONTAINING 5.4 PARTS N,N′-DI-SEC-BUTYLBENZIDINE AND 1 PART WAX, UNDER 20 PER CENT ELONGATION

Temperature, 25° C ozone flow rate, 2.52×10^{-8} mole per min (36 pphm)

Run	Ozone absorbed, mole	Accumulated ozone, mole	Running time, hr	Idle time, hr	Running time equivalent of idle time, hr	Total time, accumulative, hr
1	176.30×10^{-8}	176.3×10^{-8}	2.6	—	—	2.6
2	78.50	254.8	1.3	18.08	0.67	4.57
3	89.30	344.1	2.6	0.54	0.21	7.38
4	115.38	459.5	3.7	117.07	1.13	12.21
5	56.55	516.0	1.78	94.30	0.83	14.82
6	38.20	554.2	0.9	17.33	1.6	17.32
7	30.91	585.1	1.76	0.37	0.28	19.36
8	24.72	609.8	0.38	68.93	2.08	21.82
9	21.61	631.5	0.35	0.22	0.05	22.22
10	4.14	635.6	0.23	0.47	0.20	22.65
11	7.25	642.8	0.34	0.42	0.18	23.17
12	27.11	669.9	0.80	43.63	2.23	26.20
13	4.05	674.0	0.53	0.57	0.23	26.96
14	26.10	700.1	1.62	0.91	0.60	29.18
15	55.44	755.5	1.96	17.40	3.67	34.81
16	32.05	787.6	2.66	70.03	1.78	39.25
17	30.87	818.5	2.36	22.50	1.98	43.59
18	5.13	823.6	0.48	0.52	0.30	44.37
19	15.88	839.5	0.73	19.53	1.77	46.87
20	12.12	851.6	2.47	0.67	0.25	49.59
21	25.21	876.8	1.86	47.11	2.87	54.32
22	39.61	916.4	2.17	67.25	4.97	61.46
23	18.92	935.3	1.66	0.44	0.10	63.22
24	43.28	978.6	5.03	19.22	2.30	70.55
25	38.79	1017.4	1.94	187.52	6.62	79.11
26	16.30	1033.7	1.71	0.74	0.17	80.99
27	34.55	1068.3	5.00	18.08	0.88	86.87
28	12.60	1080.9	1.27	20.62	1.17	89.31
29	2.11	1082.9	0.10	0.54	0.17	89.58
30	40.23	1123.2	2.78	67.50	4.92	97.28
31	22.36	1145.6	3.60	19.50	0.90	101.78
32	17.64	1163.2	1.40	19.50	1.93	105.11
33	12.19	1175.4	0.95	1.50	1.22	107.28
34	23.28	1198.7	3.23	21.17	1.01	111.52
35	47.09	1245.8	2.91	92.52	5.30	119.73
36	5.01	1250.8	0.85	0.56	0.12	120.70
37	28.20	1278.9	2.44	19.25	2.32	125.46
38	2.50	1281.5	0.84	0.66	0.03	126.33
39	20.13	1301.6	1.63	20.31	1.85	129.81
40	5.88	1307.5	1.28	0.62	0.10	131.19
41	20.23	1327.7	2.11	44.68	1.95	135.25
42	8.23	1335.9	1.52	0.47	0.10	136.87
43	44.50	1380.4	3.52	91.97	5.30	145.69
44	22.14	1402.6	1.27	19.42	2.15	149.11
45	14.29	1416.9	2.73	0.54	0.10	151.94
46	38.98	1455.8	4.45	19.87	2.37	158.76
47	30.43	1486.2	4.55	19.08	1.12	164.43
			92.35	1314.11	72.08	

in 36 min of exposure, this specimen showed a sixfold increase in the absorption of ozone.

The oil-extended vulcanizates S64D, S64E, and S64E1, which each contained 1 part wax, gave rates of absorption of ozone as shown in Figure 4. It appeared that the wax, with the aid of the oil or plasticizer, had enabled such ozone sensitive materials as N-phenyl-2-naphthylamine and N-cyclo-hexyl-2-benzothiazolyl sulfenamide to migrate to the surface where a reaction with ozone took place. On the other hand, the later portions of the absorption curve can readily be extrapolated back to an initial value of zero. In all the cases when SBR vulcanizates containing no antiozonant in their formulation were subjected to a stress, there appeared to be an induction period of several minutes before the reaction of ozone with the rubber polymer can reach maximum rate of oxidation. When the maximum rate had been reached ozone cracks appeared on the surface of the specimen.

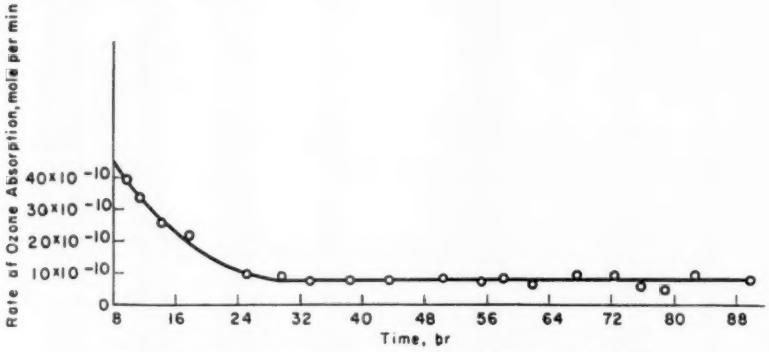


FIG. 5.—End rate of absorption versus time for successive runs—rod S12B68.

The vulcanizates S12B and S47B showed a striking difference in the absorption of ozone produced by the addition of such antiozonants as N,N′-di-*sec*-butylbenzidine or N,N′-bis[1-isobutyl-3-methylbutyl]-*p*-phenylenediamine; the high initial rate of absorption (Figure 3) followed by a rapid decline to very low values supports the findings of Shaw et al.[5] who found that antiozonants gave excellent protection to SBR vulcanizates in accelerated and outdoor tests. No cracks could be found on the surface on these specimens in several hours of exposure.

A number of SBR vulcanizates which included both an antiozonant and wax in their formulation were placed under static stress and exposed to ozone at low concentrations (30 pphm) intermittently for extended periods of time without obtaining any ozone cracks on the surface of the rods. In particular, vulcanizates S12B68 and S47A3B7 were completely protected by the antiozonant that each contained; no ozone cracking could be detected in over 100 hr for S12B68 (Table III) and over 60 hr for S47A3B7. In all cases it was found that the initial rates of absorption of ozone were high (nearly 100 per cent removal of the ozone from the ozone-air stream), but the rates gradually declined as a residue of oxidized products accumulated on the surface of the rod. During the idle time between successive exposures, it was found that fresh ozone-sensitive materials had effused to the surface of the rods so that the initial rate

of absorption in each successive run was higher than the end rate of the preceding run. After a certain number of runs, a steady state of absorption of ozone was reached in which the rate of absorption (after a few initial higher rates) became constant for a given vulcanizate. The end rates of absorption versus time for vulcanizate S12B68 are shown in Figure 5. In practice it was found that if the quantity of ozone absorbed were plotted against the corresponding time, a curve was obtained for each run which could be assembled into a composite curve as shown in Figure 6(*a*), (*b*) and Figure 7.

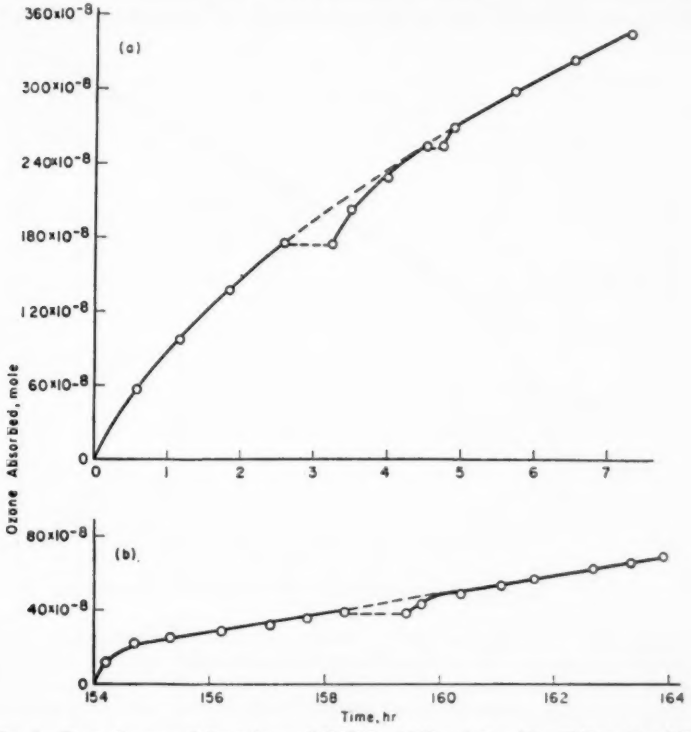


FIG. 6.—Composite curve of absorption—rod S12B68. (*a*) Runs 1, 2, and 3. (*b*) Runs 46 and 47.

In this manner the effect of the increased initial absorption in each run (due to an idle period preceding the run) was incorporated into a composite curve of ozone absorption, either by carefully matching curves or by calculation. Each composite curve shows two distinct phases in the absorption of ozone by a given specimen under the conditions of constant temperature and constant ozone pressure: phase A is initially a variable rate phase in which the quantity of ozone absorbed declines with time until phase B, a constant rate phase, is reached, wherein the rate of absorption of ozone becomes fixed.

The vulcanizate S64DB, which contained a naphthenic processing oil as an extender, gave similar results to those discussed above, except that ozone

cracking (a few fine cracks) occurred after 26 hr exposure. Vulcanizate S64BE, containing trioctyl phosphate as a plasticizer, absorbed ozone at a continuously high rate of about 85 per cent of the total ozone flowing around the specimen for 13.5 hr. Cracks appeared in 2.4 hr exposure. It is likely that the gaseous ozone dissolved to some extent into the oil phase of the rubber; this would account for the very severe attack by ozone on the vulcanizate. It was also found that when the ozone concentration was increased to about 300 pphm on any vulcanizate that contained only 3 to 5 parts of the antiozonant, very little protection was afforded the vulcanizates. The vulcanizates S64DA and S64ED, into which the antiozonant was introduced by dip coating from a 50

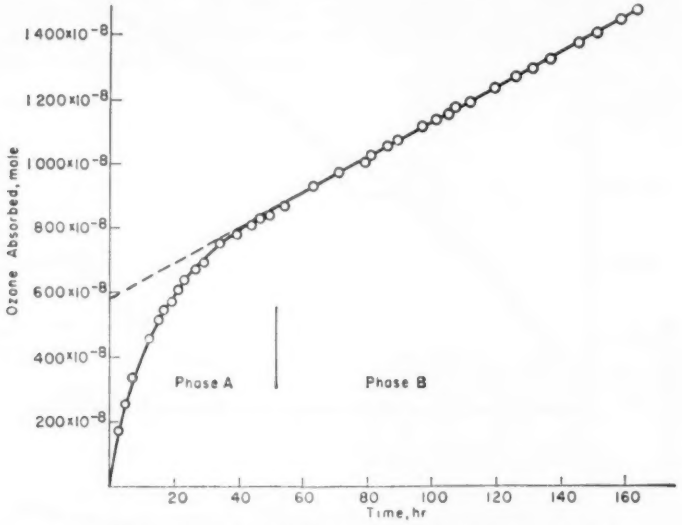


FIG. 7.—Accumulative ozone absorbed verus accumulative time—rod S12B68.

per cent solution of the antiozonant in acetone, were well protected, even at high concentrations. It was found that this protection was due to an initial increase of the antiozonant (about sevenfold) on the surface of the vulcanizate. A summary of the results obtained on the vulcanizates of series S64 is given in Table IV.

Dynamic stress.—The vulcanizates S12B46 and S12B68 were extensively studied under a dynamic stress using conditions similar to those employed in the static stress studies. In all cases it was found that the rate of absorption of ozone was about five times greater for vulcanizate S12B68 which contained the antiozonant N,N′-di-*sec*-butylbenzidine and wax, and about ten times greater for vulcanizate S12B46, which contained the same antiozonant but no wax. The results obtained on the vulcanizate S12B68 under dynamic stress are of particular interest (Table V and Figure 8(*a*) and (*b*) since two distinct points of inflection occur in the rate of absorption of ozone; one point occurs at 13.5 hr of exposure and the second point occurs at 51 hr when a steady state of absorption was reached. The first point can be taken to indicate the initial

TABLE IV

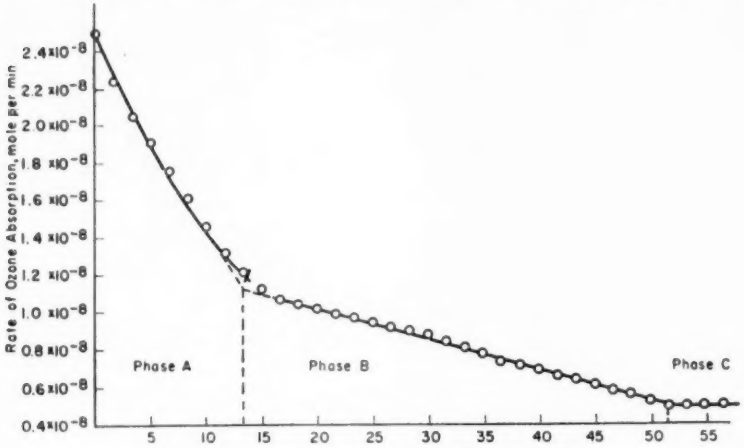
COMPARATIVE DATA ON THE OZONE ABSORPTION BY SBR RUBBER RODS—SERIES S64

Vulcanizate	Ozone pressure, atmos	Exposure time up to first cracks, hr	Accumulated ozone absorbed at first cracks, mole	Absorption rate at first cracks, mole	Value of constant rate at equilibrium stage, mole	Estimated quantity of antiozonant in surface, mole per sq in.	Remarks
S64B	2.02×10^{-7}	none at 19.3	116×10^{-7} (no cracks)	—	0.08×10^{-8}	8.3×10^{-7}	Well protected
S64B54	2.0	2.3 (stopped at 3.2 hr)	22.2	0.94×10^{-8}	0.34 (continually decreasing)	2.7	Only fair protection due to lower initial concentration of antiozonant on surface
	17.2	0.4	12.3	2.5	(continually decreasing)	2.0	No protection
S64BE	2.0	2.4	28.0	2.2	2.2 (constant)	none	Zero initial absorption rising to constant rate
S64B54E	2.2	no cracks at 2.7 hr	35.1 to 2.7 hr	0.92	—	5.1	Good protection
	17.2	0.83	31	0.20	—	3.9	Poor protection
S64E1	1.9	0.65	42.5	1.19	1.53	trace	Zero initial absorption rising to constant rate
	17.4	immediately	—	—	11.9	none	Zero initial absoprtion rising to constant rate
S64E	2.3	0.58	54	1.82	1.9	none	Zero initial absorption rising to constant rate
	17.3	immediately	—	—	13.1	none	Zero initial absorption rising to constant rate
S64DB	2.4	26	73.9	0.06	0.06	8.3	Good protection
	15.0	0.55	159	18.3	44.3	—	Poor protection
S64B54E1	1.86	no cracks	—	—	0.17	7.2	Good protection
	17.2	0.76	45.9	5.7	4.4	4.2	Poor protection
S64DA	2.2	no cracks at 23 hr	—	—	2.4	70	Very good protection
	24.0	no cracks at 10.6 hr	—	—	0.5	70	Very good protection
S64EB	2.2	20.0	333	—	2.74	110	Good protection
	150.0	uncertain	—	—	0.7	110	Surface developed a varnished appearance

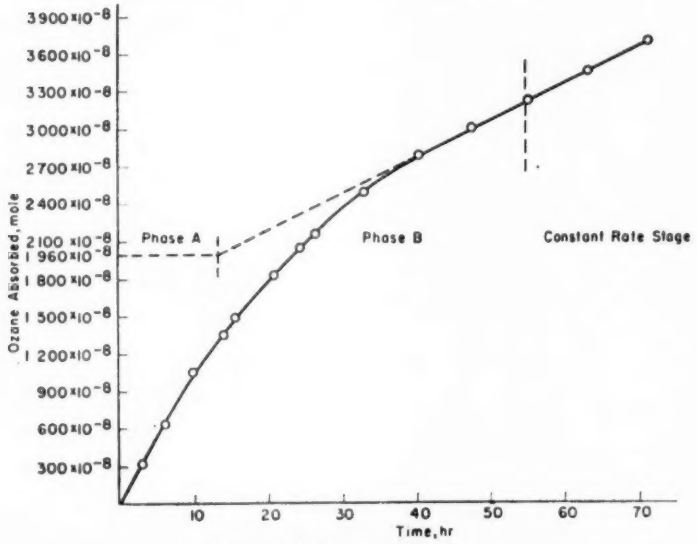
attack of ozone on the rubber polymer itself, although no cracks were visible under 32× magnification until after 30 hr of exposure.

DISCUSSION

The results show that SBR vulcanizates containing no antiozonants are readily attacked by ozone. If such vulcanizates are in a relaxed state, a film



(*a*) A composite curve of all the rate of absorption curves.



(*b*) Ozone absorbed versus accumulative time.

FIG. 8.—SBR rod S12B68 under dynamic stress.

TABLE V

DATA ON OZONIZATION OF SBR RUBBER ROD (S12B68) CONTAINING 5.4 PARTS N,N'-DI-SEC-BUTYLBENZIDINE AND 1 PART WAX AND UNDER 20 PER CENT ELONGATION—DYNAMIC STRESS

Run number	Ozone absorbed, mole	Accumulated ozone, mole	Running time, hr	Idle time, hr	Running time equivalent of idle time, hr	Total time, accumulative, hr
1	323.5×10^{-8}	323.5×10^{-8}	3.27	—	—	3.27
2	311.5	635.0	2.66	2.36	—	5.93
3	410.9	1045.9	4.14	12.87	—	10.07
4	322.6	1368.5	4.11	20.10	—	14.18
5	115.4	1483.9	1.35	4.32	0.18	15.71
6	352.2	1836.1	4.98	278.57	0.32	21.01
7	202.6	2038.7	3.12	18.55	0.37	24.50
8	122.9	2161.6	2.02	0.31	0.20	26.72
9	336.8	2498.4	5.87	18.23	1.05	34.02
10	285.2	2783.6	5.61	18.30	1.05	40.30
11	211.6	2995.2	4.51	19.54	2.40	47.21
12	223.6	3218.8	5.94	66.03	1.90	55.00
13	239.8	3458.6	4.99	739.25	3.35	63.39
14	226.7	3685.3	4.46	91.50	3.45	71.30
			57.03	1289.93		

of ozonized products is formed which eventually provides an effective barrier against any further reaction with gaseous ozone at low concentration. On the other hand if such vulcanizates are subjected to a stress, by stretching for example, the film ruptures and the reaction continues. This quickly results in a scission of the polymer chains at any points of unsaturation or sulfur linkages in the surface which gives rise to the phenomenon known as ozone cracks. As these cracks are formed, they tend to relieve the stress in the surface layers of the rubber in the locality of the cracks and thus permit the film barrier to become effective. Such is not the case in the bottom of the crevices; here the rubber is still under stress (if the specimen is under stress) and a reaction with ozone continues which permits the cracks to grow.

In the case when a vulcanizate contains an antiozonant, a much better protection is obtained against the attack by ozone, even when the rubber is under severe stress. This appears to be due (*a*) to the specific reaction of ozone with the antiozonant, (*b*) to the initial concentration of ozone-sensitive materials (chiefly the antiozonant) on the surface of the rubber which can form a film barrier of oxidized residue, and (*c*) to a continual migration of fresh antiozonant from within the rubber to the outer surface of the film. The rate at which the antiozonant migrates is probably dependent on several factors, such as its solubility in the rubber polymer, its molecular weight, and its vapor pressure in the vulcanizate. The incorporation of a small amount of wax in the rubber appears to give a higher initial concentration of the antiozonant on the surface, which gives a better film barrier of oxidized residues.

In general, one can assume that the rate of the migration of the antiozonant is proportional to its effective concentration gradient between the antiozonant in the rubber and the antiozonant on the surface of the film barrier itself. It is also dependent on temperature. The rate of ozonization of the ozone-sensitive materials is proportional to the concentration of these materials on the surface at a given time; the rate is also proportional to the partial pressure of the ozone upon the surface of the vulcanizate.

On the basis of these arguments, the following mechanism for the reaction of ozone with SBR vulcanizates is proposed:

1. The rate of migration of the antiozonant is

$$\frac{dc}{dt} = k_1 C_i$$

where C_i is the effective concentration of the antiozonant in the rubber.

Since C_i remains substantially unchanged, the rate equation is simply

$$\frac{dc}{dt} = K_1 \text{ (a constant)} \tag{1}$$

2. The rate of ozonization on the surface layer is

$$-\frac{dc}{dt} = k_2 \cdot C_t \cdot p_{o_3}{}^n \cdot 1/S$$

where C_t is the concentration of the ozone-sensitive material at time t, $p_{o_3}{}^n$ is the partial pressure of the ozone, raised to some power which is dependent on the stoichiometry of the chemical reaction, and S is the thickness of the oxidized film.

Since the partial pressure of the ozone was held constant in each experimental run and since it can be assumed that when a steady state has been reached the thickness of the oxidized film increases very slowly, depending on K_1 in Equation (1), the rate equation reduces to the pseudo-unimolecular form:

$$-\frac{dc}{dt} = K_2 \cdot C_t, \quad \text{where } K_2 = k_2 \cdot p_{o_3}{}^n \cdot 1/S \tag{2}$$

3. When a steady state has been reached (phase B of Figure 7), the rate of migration, in equivalents of ozone, is equal to the rate of ozonization:

$$\frac{dc}{dt} \text{ (of migration)} = -\frac{dc}{dt} \text{ (ozonization)} \tag{3}$$

Equation (2) is better expressed in the usual alternate form:

$$-\frac{dc}{dt} = -\frac{d(a-x)}{dt} = K_2 \cdot C_t$$

where a is the initial concentration of the ozone-sensitive materials on the rubber surface and x represents the decrease up to time t. Then $C_t = (a - x)$ at time t. Finally $\frac{dx}{dt} = K_2 (a - x)$ which, upon integration, gives

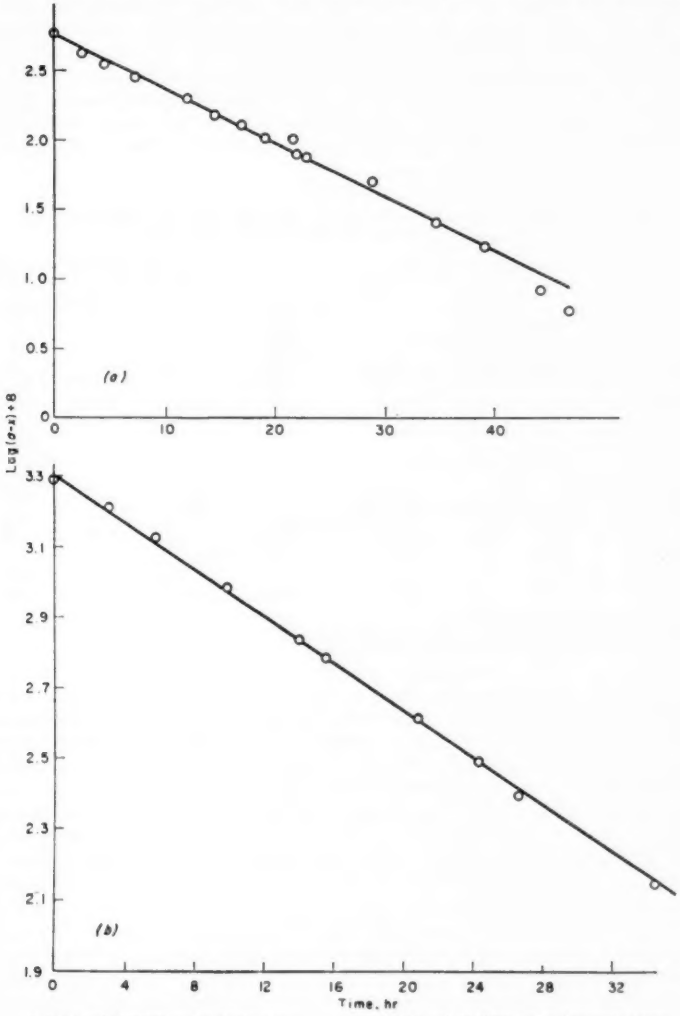
$$\log (a - x) = -\frac{K_2}{2.303} t + \log a \tag{4}$$

However C_t also depends on the amount of fresh antiozonant which has migrated to the surface of the rubber during the time t, and this amount is equal to

K_1t. Hence Equation (4) should be modified to the form:

$$\log (a + K_1t - x) = (- K_2/2.303)t + \log a \qquad (5)$$

Since the reaction of ozone with the ozone-sensitive materials on the rubber surface was followed experimentally by measuring both the rate of absorption



(*a*) SBR rod S12B68 under static stress. (*b*) SBR rod S12B68 under dynamic stress.

FIG. 9.—Log $(a-x)$ versus time. From equation $\log (a-x) = \left(\frac{-K_2}{2.303}\right) t + \log a$.

of ozone and the quantity of ozone absorbed in each run, no direct determination of the concentrations of the antiozonant or other ozone-sensitive materials were made. Such concentrations, however, are directly proportional to the quantity of ozone which reacts.

Therefore, in Equation (5), the term a is the initial concentration of the ozone-sensitive materials on the rubber surface expressed in terms of the moles of ozone to which these materials are equivalent. The value of a for the vulcanizate S12B68 under static stress is found by extrapolating the straight-line portion of phase B in Figure 7 to zero time. The value of x at any time, t, is equal to the moles of ozone absorbed up to time t, minus K_1t, since K_1t is the amount of fresh antiozonants which has migrated to the surface. K_1 (Equation (1)) is equal to 5.4×10^{-8} mole ozone per hr per 6.6 sq cm for phase B. A test was made to see whether Equation (5) applies to phase A of the curve

TABLE VI

DATA ON OZONE ABSORPTION BY SBR RUBBER RODS CONTAINING AN ANTIOZONANT, UNDER 20 PER CENT ELONGATION

Description						Value of constants for equation $\log (a+k_1t-x) = -K_2t/2.303 + \log a$		
	Antiozonant		Wax, parts per 100 parts hydrocarbon		Ozone flow rate, mole per min			
Rod number	Name	Concentration		Type of stress		K_1 mole per hr	K_2 hr^{-1}	a mole
S12B68	[a]	5.4	1	Static	2.52×10^{-8}	5.44×10^{-8}	0.092	590×10^{-8} (6.56 sq in of surface)
S12B46	[a]	5.4	none	Dynamic	2.52	64.2	—	521
S12B68	[a]	5.4	1	Dynamic	2.52	28.7	—	1960
S47B	[b]	3.0	none	Static	7.04	3.6	1.25	68
S47A3B7	[b]	3.0	1	Static	7.5 2.5	1.8	0.11	675
S46B	[c]	3.0	1	Static	2.86	5.22	0.23	448

[a] N,N′-di-*sec*-butylbenzidene.
[b] N,N′-bis(1-isobutyl-3-methylbutyl)-p-phenylenediamine.
[c] N,N′-bis(1-ethyl-3-methylbutyl)-p-phenylenediamine.

in Figure 7 by calculating the values of $(a - x)$ for the first 15 runs on the rod S12B68, under static stress. The value for log $(a - x)$ were plotted against the corresponding times and gave a straight line (Figure 9(*a*)), indicating good agreement of the data with the proposed equation. The value of the specific rate constant, K_2, was found to be 0.092 reciprocal hour.

In the application of the rate equation to the curve obtained from the measurements of the ozone absorbed by the vulcanizate S12B68, under dynamic stress, it is necessary to account for the additional absorption brought about by the attack by ozone on the rubber as well as its reaction with the antiozonant. From the distinct change in the rate of absorption at 13.5 hr in the curve shown in Figure 8(*a*), it was assumed that at this point the attack on the rubber was initiated. It was also assumed that the rate of migration of the antiozonant in this case was substantially the same as for the rod S12B68 under static stress. It was found that the values of $(a - x)$ could be calculated in the following way: The initial value of the ozone-sensitive material on the surface exposed to ozone was found by extrapolating the constant rate portion of the

curve (Figure 8(*b*)) to the point at 13.5 hr and taking the value of 1960 $\times$ 10^{-8} moles directly opposite the ordinate. This is permissible if it is assumed that the rubber was not attacked until 13.5 hr had elapsed. The slope, K_1, of the straight portion of the curve is 28.7 $\times$ 10^{-8} mole ozone per hr and is the sum of the two rates, k_1, and k_2, where k_1 is the rate of migration of the antiozonant in equivalents of ozone (5.4 $\times$ 10^{-8} mole per hr) and k_2 is the rate of ozonization of the rubber surface beginning in phase B at 13.5 hr. The value of $(a - x)$ is equal to $a + k_1t - Y_t$ for phase A. At the beginning of phase B at 13.5 hr a term 23.3 $(t - 13.5) \times 10^{-8}$ added to account for the ozone which has reacted with the rubber, at the time t beyond 13.5 hr. The value of k_2 is 23.3 $\times$ 10^{-8} and Y_t is the total ozone consumed at time t.

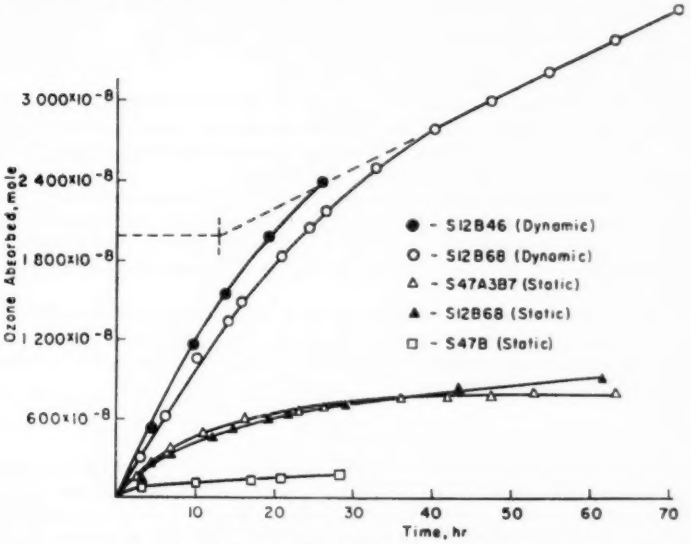


FIG. 10.—Ozone absorbed by SBR rubber rods under stress.

The values for $(a - x)$ were calculated for the first eight runs and, when plotted against the corresponding times, gave a straight line (Figure 9(*b*)), thus indicating good agreement of the data with the proposed equation. From these results it is evident that the rates of migration of the antiozonant in the vulcanizate S12B68, are substantially the same whether the specimen is under static or dynamic stress.

A summary and comparison of quantities of ozone absorbed by the various vulcanizates investigated is given in Table VI and Figure 10.

SUMMARY

All SBR vulcanizates, when tested in a relaxed state, reacted with ozone of low concentrations to form a film of oxidized products which provided an effective barrier against further attack by gaseous ozone.

SBR vulcanizates that were under stress, but which contained no effective antiozonant in their formulation, were readily attacked by ozone. The absorp-

tion of ozone appeared to begin with an initial rate of zero which was followed by rapidly increasing rates until a maximum had been reached, when ozone cracks were visible on the surface of the rubber.

SBR vulcanizates that were under stress, but which contained an antiozonant, were protected from an attack by ozone to a degree that ranged from poor to excellent. The degree of protection depended (*a*) on the differential in the rates of reaction of the antiozonant and the rubber hydrocarbon with ozone, (*b*) on the initial concentration of the antiozonant on the surface of the vulcanizate which reacted with ozone to form a barrier of oxidized residues, and (*c*) on the rate of effusion of fresh antiozonant from within the rubber to the outer surface of the barrier.

SBR vulcanizates containing a naphthenic processing oil as an extender were not so resistant to ozone as standard SBR vulcanizates. It is probable that the effectiveness of the antiozonants tested in these vulcanizates was reduced by their high solubility in the oil phase.

SBR vulcanizates containing trioctyl phosphate as a plasticizer were vigorously attacked by ozone. It is possible that the gaseous ozone dissolved to some extent into the plasticizer phase, increasing the concentration of ozone in the area causing a more severe oxidation of the rubber.

SBR vulcanizates that had been coated with an antiozonant by dipping the specimen several times into a solution of the antiozonant in a solvent were found to contain a higher concentration of the antioxonant directly on the surface of the vulcanizate than in the case where three parts of the antiozonant were added during vulcanization.

A mechanism for the ozonization of SBR vulcanizates has been proposed which includes a possible mechanism for the protective action of antiozonants. A rate equation has been derived from this mechanism which was consistent with the experimental rate data.

SYNOPSIS

All styrene-butadiene rubber (SBR) vulcanizates, when tested in a relaxed state, reacted with ozone (25 to 500 pphm (parts per hundred million) ozone in air) to form an oxidized film which provided an effective barrier against attack.

SBR vulcanizates that were under stress, but which contained no effective antiozonant in their formulation, were readily attacked. The absorption of ozone began with an initial rate of zero but rapidly increased until a maximum rate had been reached when ozone cracks became visible.

SBR vulcanizates that were under stress, but which contained an antiozonant, absorbed ozone with a high initial rate which depended on the concentration of the ozone-sensitive materials on the surface of the vulcanizate and on the partial pressure of the gaseous ozone. The rate of absorption declined during the exposure time until a steady low equilibrium rate was reached. The vulcanizates were protected from an attack by ozone (cracking) to a degree which ranged from poor to excellent, and depended (*a*) on the differential in the rates of reaction of ozone with the antiozonant and the rubber hydrocarbon, (*b*) on the initial concentration of the antiozonant at the surface of the vulcanizate, and (*c*) on the rate of effusion of fresh antiozonant from within the rubber to the outer surface of the oxidized barrier.

A mechanism is proposed for the protective action of antiozonants in vulcanizates, and a rate equation has been derived from this mechanism which is consistent with the experimental data.

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COMPARISON OF ACCELERATED AND NATURAL TESTS FOR OZONE RESISTANCE OF ELASTOMERS *

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The destructive action of ozone on vulcanized rubber has been known for a long time. As far back as November, 1868, Samuel F. B. Morse complimented Austin Goodyear Day for his "Kerite" insulation because it had been found to resist the deteriorating effects of the ozone of the atmosphere[1]. However, it was not until the publication of the work of Williams[2] in 1926 and that of Van Rossem and Talen[3] in 1931 that the role of ozone in the weathering of vulcanized rubber was clarified. These workers found that the multiple cracking which occurs on stretched rubber on outdoor exposure is caused by the ozone in the atmosphere and not by the effects of light. R. G. Newton[4] confirmed this conclusion in 1945. In 1946, Crabtree and Kemp[5] also confirmed the conclusion and later described an accelerated ozone weathering test for rubber[6]. This method has been published as ASTM Method D 1149 (Tentative Method of Test for Accelerated Ozone Cracking of Vulcanized Rubber (D 1149-55T), Part 6, p. 1162) and fundamentally involves exposure of specimens under stress to a controlled concentration of ozone in air at a definite temperature. This review is solely concerned with comparisons of ozone resistance found by such tests with that found by exposure outdoors. It is proposed to discuss accelerated and natural tests, compare results obtained in the two types of tests and then attempt to draw some conclusions.

ACCELERATED TESTS

General.—The accelerated tests to be considered are limited to those involving ozone concentrations below 1000 parts per hundred million parts (pphm) of air and temperatures not exceeding 150° F. Ozone concentrations in this range are usually obtained by passing air over quartz lamps.

Apparatus.—While many laboratories have devised and used apparatus of their own design as for example Ford and Cooper[7], some have duplicated the Crabtree-Kemp design while others have acquired commercially available units. Three of the latter are included in the descriptions which follow.

The Crabtree-Kemp apparatus is usually a cylindrical chamber with a capacity larger than 6 cu ft. Ozone is generated by a controlled quartz lamp located below a baffle near the bottom of the chamber. A ring heater or glow coil is provided for heating. Air flow is mostly by convection aided by a small exhaust fan located in a chimney built into the cover. An essential feature is the method used for determining ozone concentration. The chambers are usually operated at an ozone concentration of 25 to 50 pphm and at temperatures from 90 to 120° F.

The G. F. Bush Ozonator, model C1, consists of an insulated cylindrical exposure chamber with a capacity of 1 cu ft and a control panel. Ozone sam-

* Reprinted from "*Symposium on Effect of Ozone on Rubber*," ASTM Special Technical Publication No. 229, pages 88–96, September, 1958.

pling apparatus is built into the control panel. Ozone concentration can run from 10 to 500 ± 2 pphm and temperature may be maintained from ambient to 200° F. Throughput of ozone in the chamber and titration apparatus is obtained with a 1½ cu ft per min capacity vacuum pump.

The Mast Model 700-1 Ozone Test Chamber includes an exposure chamber, ozone generator, pumps, and titration apparatus as one integral unit. The exposure chamber is rectangular and has a capacity of 5.7 cu ft. A compressor brings ozonized air to the chamber where a recirculation blower provides circulation over the samples. Ozone concentration can be varied from 15 to 1000 pphm. Temperatures from 5° F below ambient to 150° F can be maintained.

The apparatus of Gabuzda and Hannaway features generation of ozone by passing dry air into a quart jar in which an ultraviolet lamp is suspended. Four generating units are provided and the tubing is arranged so that one, two, three, or all four generators may be used. Each lamp has its individual control and the result is that ozone concentration may be varied within wide limits. The ozonized air is led to a rectangular Lucite chamber. There is no provision for temperature control nor is there any apparatus for ozone titration. When this apparatus was used at an ozone concentration of 300 to 400 pphm, it was found that a satisfactory estimation of ozone could be made by reading the color of the potassium-iodide solution in a Klett-Summerson photoelectric colorimeter.

Types of specimens.—Sheet specimens.—Rectangular or wedge-shaped strips and dumbbells are cut from standard molded test sheets. The wedge strips and dumbbells are mounted under horizontal stretch. The rectangular strips may also be mounted under horizontal stretch but sometimes are mounted as bent loops according to method B of ASTM Method D 518-44 (Method of Test for Resistance to Surface Cracking of Stretched Rubber Compounds (D 518-57T), 1955 Book of ASTM Standards, Part 6, p. 1167). In addition, rectangular strips may be bent around mandrels of a size to give the desired stress.

Molded specimens.—(*a*) Triangular specimen, ¾ in. base, ½ in. altitude (Figure 1, Tentative Method of Test for Weather Resistance Exposure of Automotive Rubber Compounds (D 1171-57T), 1957 Supplement to Book of ASTM Standards, Part 6, p. 248). These may also be extruded; (*b*) DeMattia (Figure 3, Tentative Method of Test for Resistance of Vulcanized Rubber or Synthetic Elastomers to Crack Growth (D 813-57T), 1957 Supplement to Book of ASTM Standards, Part 6, p. 197).

Extruded specimens.—These include wire and cable specimens which are bent around mandrels to give the desired stretch.

Miscellaneous specimens.—These include specimens cut from actual parts, such as tire treads and carcasses, gloves, molded parts, etc.

Ozone concentration and temperature.—Ozone concentration ranges from 25 to 500 pphm. Temperatures range from ambient to 120° F.

NATURAL TESTS OR OUTDOOR TESTS

Types of specimens.—Specimens for outdoor exposure are similar to those used for the accelerated tests.

Method of exposure.—Specimens mounted on weatherproof panels were usually exposed in racks at ground or roof level. Panels are inclined 45 degrees to the horizontal and face south.

Locations.—A good many outdoor exposures are made at plant sites wherever they may be. However, several locations are chosen for reasons as listed below:

1. Los Angeles, Calif.—High ozone,
2. Yuma, Ariz.—Ozone normal, but temperature is high, and
3. Florida—Ozone normal, temperature moderately higher than most of rest of U. S.

COMPARISON OF RESULTS OBTAINED IN ACCELERATED AND OUTDOOR EXPOSURE TESTS

General.—A major difficulty in making comparisons between natural and accelerated tests arises from the fact that widely varying results can be obtained in natural tests[8]. The location of the test site as well as the season of the year will influence results, especially in stocks having border-line resistance. Another difficulty is duration of exposure. While a month or two may be adequate to screen out stocks with moderate ozone resistance, longer periods are required as resistance increases.

From a practical standpoint, a stock that develops many very fine cracks may be considered better than one which develops a few very large cracks. However, in the comparisons which follow, degree of cracking is not considered. In view of the number of rating systems in use and the fact that assignment of ratings within the systems depends on the judgment of the observer, comparisons including degree of cracking would only add confusion. Therefore any degree of cracking is considered a failure. Only those stocks are included which show no cracking in at least one of the exposure conditions. Details of protective systems or other compounding variations are excluded as being beyond the scope of this review.

Survey of literature.—Until a short time ago, although some workers had reported results on outdoor or sunlight aging of elastomers, very little had been published on outdoor *versus* accelerated aging of elastomers. Recently under the impetus of Rock Island and Detroit Arsenals, a tremendous amount of work has been done on this subject, and reports are becoming available. Results from several of these reports are included in the summaries which follow:

Winkelmann: static exposure testing of automotive compounds[8].—Automotive compounds, presumably based on SBR, were exposed in an ozone chamber maintained at 100° F and 25 pphm ozone for 70 hr and outdoors at Clearwater and Miami, Fla., and at Chicago, Ill., for 30 days. The data do not lend themselves to analysis since they are given in terms of comparison of degree of cracking at the various exposures and the behavior of individual specimens in the exposures is not listed.

Winkelmann concluded that while the accelerated ozone test was more severe than a 30-day outdoor exposure, over 20 per cent of the specimens showed more cracking outdoors than in the ozone chamber. It would be possible to select compounds on the basis of ozone chamber tests that would not show up well on outdoor exposure.

R. E. Thompson, Jr., F. J. Presock, and W. B. Dunlap, Jr., Lee Rubber and Tire Corp.[9].—This work was concerned with the development of ozone resistant tires and mechanical items. Most of the stocks were based on SBR low temperature polymer. Some terpolymers were included along with a few neoprene and NBR stocks. The base test recipe was an SBR tread type compound with 50 parts per hundred parts of rubber hydrocarbon black loading. The test program was extensive. It included dynamic as well as static exposure to ozone and static exposure outdoors. Static exposures were made at three elongations. All tests were repeated after specimens had been aged.

TABLE I

SUMMARY OF RESULTS

620 Specimens—Lee Rubber and Tire Co.

			Specimens which did not crack	
			Number	Per cent
Dynamic exposure		New	118	19.0
		Aged	79	12.7
Outdoor static exposure at three elongations	11 per cent	New	356	57.4
		Aged	325	52.4
	26 per cent	New	223	35.9
		Aged	188	30.3
	56 per cent	New	137	22.0
		Aged	114	18.4
Accelerated ozone static exposure at three elongations	11 per cent	New	311	50.1
		Aged	305	49.2
	26 per cent	New	198	31.9
		Aged	153	24.7
	56 per cent	New	96	15.5
		Aged	—	—

Details of tests.—(*a*) *Specimens.*—(1) For dynamic tests, standard 1 by 6 in. De Mattia specimens (ASTM Tentative Method D 813); (2) For static tests, De Mattia specimens cut in half (0.5 by 6 in.).

(*b*) *Elongation.*—(1) For dynamic test: 263 cpm, $\frac{5}{32}$ in. stroke giving 26 per cent elongation at the base of the groove; (2) For static tests, 11, 26, and 56 per cent at the base of the groove.

(*c*) *Ozone concentration.*—(1) For dynamic test: 540 pphm; (2) For static test: 250 pphm.

(*d*) *Temperature of accelerated tests: 100° F.*

(*e*) *Duration of tests.*—Dynamic −100,000 cycles; (2) Static Ozone Test: 48 hr; (3) Outdoor Exposure Tests: 40 days.

While specimens from 643 compounds were tested, the summaries given in Tables I, II, and III include only the 620 specimens on which information was complete.

TABLE II

DYNAMIC VERSUS STATIC EXPOSURE

Lee Rubber and Tire Co.

	Dynamic *versus* static exposure, 26 per cent elongation		Dynamic *versus* static exposure, 11 per cent elongation	
	Number	Per cent	Number	Per cent
Pass dynamic test	118	100	118	100
Pass dynamic, outdoor and accelerated ozone tests	56	47.4	98	83
Pass dynamic and outdoor tests	14	11.8	10	8.5
Pass dynamic and accelerated ozone tests	26	22.0	8	6.8
Pass dynamic but fail outdoor and accelerated ozone test	22	18.6	2	1.7

Table I lists the numbers of specimens which passed individual tests. The results indicate that the dynamic ozone test is most severe, that more specimens pass the outdoor test than the static ozone test, and that fewer specimens survive as elongation is increased.

Table II compares dynamic ozone with static ozone and outdoor exposure on 11 and 26 per cent elongation. Even though the specimens are elongated to 26 per cent in the dynamic test, it appears that there is better correlation between the 11 per cent static and the dynamic test.

Table III summarizes the behavior of the unaged specimens in the outdoor and static ozone exposures. Correlation between the two tests is better at the lower elongation. At all elongations it is seen that more specimens pass the outdoor test. At 11 per cent elongation, 78.6 per cent of the specimens which pass the outdoor test also pass the ozone test. At 26 per cent elongation, the percentage is 65.5 and at 56 per cent elongation, the percentage is 43.0. Of the specimens which pass outdoors and fail in ozone, some may fail as outdoor

TABLE III

COMPARISON OF OUTDOOR AND ACCELERATED OZONE EXPOSURE OF UNAGED SPECIMENS

Lee Rubber and Tire Co.

	11 per cent elongation		26 per cent elongation		56 per cent elongation	
	Number of specimens	Per cent	Number of specimens	Per cent	Number of specimens	Per cent
Fail outdoor and accelerated ozone tests	264	—	397	—	483	—
Pass outdoor test	356	100	223	100	137	100
Pass accelerated ozone test	311	87.3	198	86.8	96	70.0
Pass outdoor and accelerated ozone tests	280	78.6	146	65.5	59	43.0
Pass outdoor, fail accelerated ozone test	76	21.3	77	34.5	78	56.9
Pass accelerated ozone, fail outdoor test	31	8.7	52	23.3	37	27.0

exposure is continued. Hence the real anomaly in the test is in the number of specimens which pass the ozone test but fail outdoors. These were not the same specimens for each of the elongations. At 11 per cent elongation, 31 specimens out of 311 or 10 per cent are in this category, at 26 per cent elongation there are 52 out of 198 or 26 per cent, and at 56 per cent elongation there are 37 out of 96 or 38 per cent.

The authors concluded that the testing method developed and used in the evaluation shows very good correlation between accelerated indoor tests, outdoor exposures, and final end product service.

R. F. Shaw, Z. T. Ossefort, and W. J. Touhey[10].—A considerable amount of work is reported upon here. The results do not readily lend themselves to comparison since exposure periods both outdoors and in the ozone cabinets varied widely. In this case the conclusion of the authors must suffice.

They found that the fluctuation of atmospheric ozone concentrations make outdoor exposure tests difficult to correlate with accelerated ozone cabinet tests since the reaction rate with the inhibitor is governed by the ozone concentration and the migration rate of the antiozonant to the rubber surface.

ASTM Tentative Method D 1149 apparatus (Crabtree-Kemp) was used. Ozone concentration was 25 pphm and the temperature was 100° F.

R. G. Spain, Burke Research Co.[11,12].—These two reports cover a vast amount of work. Dynamic and static ozone tests together with outdoor exposure tests in California and Florida are reported. However, it was not possible to prepare correlation tables which would cover more than a few specimens.

D. A. Meyer and J. G. Sommer, The Dayton Rubber Co.[13].—The compounds tested were mostly SBR low temperature polymer tire tread formulations including some with reclaim. 23 NBR compounds were included. The test program also included dynamic and static exposure outdoors and in ozone both before and after aging 70 hr at 212° F.

A review of the data indicated that only the unaged static outdoor and accelerated ozone tests would be useful in this review. Again, the only criterion used was cracking or no cracking, without regard to degree of cracking.

The specimens used for the tests were bent loop per ASTM Method D 518 (method B). Accelerated ozone tests were conducted at 30 and 50 pphm ozone at room temperature. The outdoor exposure site was Dayton, Ohio.

TABLE IV

COMPARISON OF OUTDOOR AND ACCELERATED OZONE EXPOSURE OF UNAGED SPECIMENS[13]

192 Specimens—The Dayton Rubber Co.

	Number of specimens	Per cent
Fail outdoor and accelerated ozone tests	103	53.6
Pass outdoor test	45	23.4
Pass accelerated ozone test	78	40.6
Pass outdoor and accelerated ozone tests	34	17.7
Pass outdoor, fail accelerated ozone test	11	5.7
Pass accelerated ozone, fail outdoor test	44	22.9

Table IV is a summary of the static exposure tests on the unaged specimens. Correlation between the two tests is not good. About 23 per cent of the specimens survived the ozone test but failed outdoors. The conditions of the accelerated ozone test were apparently too mild. A temperature higher than room temperature may have led to better correlation. However, the results of the test did provide a guide for the production of ozone-resistant tires and mechanicals.

Bell Telephone Laboratories tests.—Some of these data have been reported previously[14] but the present summary is based on somewhat longer outdoor exposures.

In these tests specimens cut from press-cured sheets were exposed either as bent loops (ASTM Method D 518, method B) or wound on mandrels to give 30 per cent stretch.

In all cases, the Crabtree-Kemp method and apparatus for ozone exposure were used. All accelerated and outdoor tests were static tests.

The first series, summarized in Table V, consisted of specimens from 94 stocks. Eight of these were neoprene jackets while the remainder were SBR jackets and insulations. 30-day exposures in the ozone chambers are compared with 3-yr outdoor exposures at Murray Hill, N. J., and at Los Angeles, Calif. From the summary given in Table V, it will be seen that correlation between accelerated and outdoor tests is better at 120° F than at 110° F. An

TABLE V

COMPARISON OF 30-DAY OZONE AND 3-YR OUTDOOR EXPOSURE OF PRESS-CURED SPECIMENS

94 Specimens—Bell Telephone Laboratories, Series I

	25 pphm ozone	
	110° F	120° F
Fail all tests	36	46
Pass all tests	27	25
Pass accelerated ozone, fail outdoors test, Murray Hill	18	6
Pass accelerated ozone, fail outdoors tests, Los Angeles	23	9
Pass outdoor test, Murray Hill; fail accelerated ozone test	5	9
Pass outdoor test, Los Angeles; fail accelerated ozone test	1	6
Pass outdoor test, Murray Hill; fail outdoor test, Los Angeles	10	—
Pass outdoor test, Los Angeles; fail outdoor test, Murray Hill	2	—

indication of the difference in severity in conditions between Los Angeles and Murray Hill is seen in the fact that 10 specimens failed at Los Angeles but survived at Murray Hill.

The second series summarized in Table VI involved 227 specimens. Of these, 65 were butyl stocks and the remainder were SBR insulations and jackets. Outdoor exposure was two years at Murray Hill. Here again, correlation is somewhat better between the outdoor and 120° F ozone test.

CONCLUSIONS

While other data are available, it is believed that the data summarized herein are sufficient to give a good average picture of results obtained in static accelerated ozone *versus* outdoor exposure tests. At The Bell Telephone Laboratories where most of the work has been with black stocks, results indicate that correlation is dependent on the base polymer in the stocks under test. Thus, in polymers which are inherently resistant to ozone, protective systems are very effective and correlation is very good. This has been true of black neoprene stocks and evidence indicates that it may also be true for butyl stocks. With natural, SBR and NBR rubbers, protection is more difficult and results vary more widely. With the introduction of the newer and more effective antiozonants such as the dioctyl-*p*-phenylene diamines, correlation is much better.

It has been argued that absolute correlation should not be expected since in outside tests there are influences affecting cracking behavior which are absent in the indoor tests. These include sunlight, rainfall, and temperature as well as ozone concentration fluctuations. It has been observed that specimens

TABLE VI

COMPARISON OF 30-DAY OZONE AND 2-YR OUTDOOR EXPOSURE OF PRESS-CURED SPECIMENS

227 Specimens—Bell Telephone Laboratories, Series II

	25 pphm ozone	
	110° F	120° F
Fail outdoors and accelerated ozone tests	156	165
Pass outdoors and accelerated ozone tests	20	23
Pass accelerated ozone, fail outdoors tests	36	25
Pass outdoors, fail accelerated ozone test	15	14

from some stocks exposed in the late fall of the year will go through the following summer without cracking, while specimens from the same stock exposed in late spring will crack in a few days. This probably results from a combination of factors. Low ozone concentration coupled with low temperature greatly reduces susceptibility to crack formation and may provide time for stress relaxation or, perhaps, for the formation of a protective coating through the effects of sunlight activated changes in the surface.

In the accelerated ozone test, temperature and ozone concentration are carefully controlled and other variables are absent. The test will at least isolate the effect of ozone which alone is responsible for cracking.

Aside from the effect of location and season of the year, there is also the question of the duration of the outdoor exposure to be used as a criterion. This may vary widely as between tires where a 4 or 5 yr period will suffice and utility or communication wires where periods in the order of 20 yr are involved.

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OZONE RESISTANCE OF ELASTOMERIC VULCANIZATES *

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The problem of obtaining rubber products (rubber is used throughout this paper in the generic sense) having adequate resistance to ozone has become more difficult in recent years principally because of the increased use of ozone-susceptible synthetic rubber, increasing use of oil extended and plasticized rubber, and the higher atmospheric ozone concentrations existing around many industrial centers. While the problem is common to all users of rubber items, it is believed to be especially acute in the case of the military, since this usage involves long periods of storage under a variety of conditions, with the mandatory requirement that the material be at all times in a state of immediate combat readiness. During these periods of uncertain global conditions, the time-consuming processes of manufacture and procurement cannot be relied upon to provide the necessary rubber for operation of a modern military machine. A typical example depicting ozone cracking resulting from static storage of a truck tire and the enlargement of these cracks after a short period of service is shown in Figure 1.

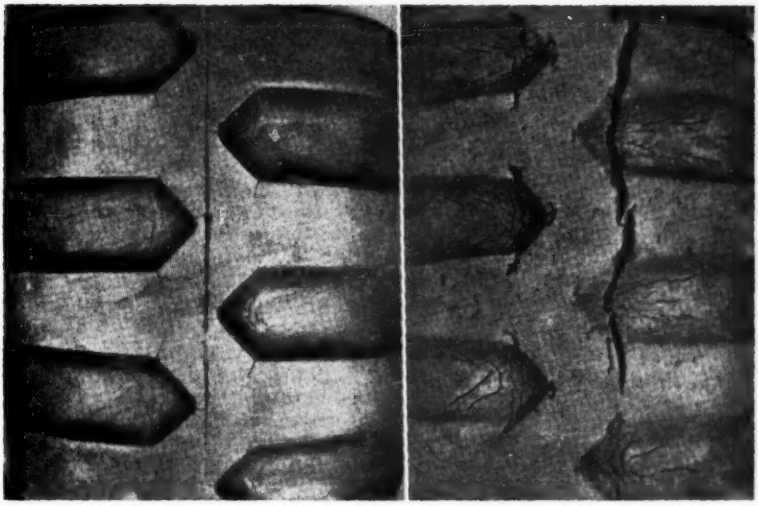
The means presently available for obtaining ozone resistance in rubber items may be classified as follows:

A. Proper selection of polymer:
   (1) Chemically saturated type, and
   (2) Sterically hindered type;
B. Application of physical barrier:
   (1) Wrappers—paper or plastic films,
   (2) Paint film—flexible films of ozone resistant rubber or plastic, and
   (3) Chemical film—antiozonant in solvent;
C. Proper compounding and use:
   (1) Chemical antiozonants,
   (2) Waxes,
   (3) High set and low modulus compounds, and
   (4) Storage of items in unstressed state.

With the notable exception of the use of chemical antiozonants[1], these methods are practically identical to those listed in *Chemistry and Technology of Rubber*[2] over 20 years ago. Of course, during this interval many additional ozone-resistant rubbers have become available, providing the compounder a much greater latitude in choice of starting material from which to prepare ozone-resistant compounds.

The resistance of rubber products to ozone cracking is known to be affected by many factors. A list of the most important of these would undoubtedly

* Reprinted from "Symposium on Effect of Ozone on Rubber", ASTM Special Technical Publication No. 229, pages 39–56. The opinions or assertions contained herein are not to be construed as being official or reflecting the views of the Department of the Army.



(*a*) 0 Miles, 5 yr static storage. (*b*) Same tire after 3052 miles of service.

FIG. 1.—Failure of truck tire due to ozone cracking.

include the following:

1. Ozone concentration;
2. Stress on specimen—dynamic or static;
3. Chemical nature of base polymer;
4. Compounding variables:
   (*a*) Presence of chemical inhibitors or waxes,
   (*b*) Type and quantity of filler, and
   (*c*) Plasticizer content;
5. Temperature of exposure; and
6. State of cure.

It will be the purpose of the present writing to elaborate on item 3 above, to classify the presently available elastomeric polymers with regard to their ozone resistance, and to describe in some detail how the ozone resistance of vulcanizates based on these polymers can be modified by compounding ingredients.

CLASSIFICATION OF ELASTOMERS ON BASIS OF OZONE RESISTANCE

All unstressed elastomers are resistant to cracking when exposed to ozone, even at quite high concentrations (10,000 to 15,000 parts per hundred million (pphm))[3–6]. It has been shown[7] that reaction with ozone under these conditions does take place but is of short duration. Apparently a microscopic layer of ozone-resistant product is formed, at and near the rubber surface, which inhibits further attack. The fact that later stressing (not in ozone) of the exposed specimens does not reveal visible cracks[32] can only be explained by the extreme thinness of the inert layer which has been formed.

It is well known that elastomers differ widely in their resistance to ozone when exposed under stress. On the basis of their ozone resistance, vulcanizates may be classified into three groups, namely:

1. Inherently ozone resistant,
2. Ozone resistant if properly compounded (without antiozonant), and
3. Ozone resistant if properly compounded (antiozonant required for maximum protection).

Before discussing the ozone resistance of these groups in detail, a few general comments regarding the methods used for testing ozone resistance will be required.

A great deal of the information in the literature regarding the ozone resistance of vulcanizates is contradictory. In many cases, this arises from improper definition of the conditions under which the tests were made and the exercise of different criteria in assessing the degree of ozone attack. Crabtree and Malm[8] have expressed the situation well when they state that there is really no satisfactory standardized test for susceptibility to ozone. This is due primarily to lack of a satisfactory and completely objective method of assessing the degree

TABLE I

INHERENTLY OZONE-RESISTANT ELASTOMERS

Chemical Name	Trade Name
Acrylic ester-acrylonitrile	Acrylons
Chlorosulfonated polyethylene	Hypalon
2-(2′-cyanoethoxy)ethyl acrylate	Vyram
Ethyl acrylate-chloroethylvinyl ether	Hycar 4021
Fluorinated silicone	LS-53
Monochlorotrifluoroethylene-vinylidene fluoride	Kel-F Elastomer
Poly(1,1-dihydroperfluorobutyl acrylate)	1F4 (Poly-FBA)
Silicone rubbers	Silicone rubbers
Vinylidene fluoride-hexafluoropropylene	Viton A

of damage. Current appraisal is based either upon the time elapsing before cracks are observable under fixed magnification or upon visual estimate of damage in comparison with a series of standards. Both procedures are subjective measures with all the defects inherent thereto. In discussing the ozone resistance of rubber compounds, it is, therefore, essential as a very minimum to state the ozone concentration, stress (static or dynamic), type sample, criterion of failure, and test temperature. In our work we have chosen as criterion for failure the time to first crack under a fixed magnification as being the least objectionable of the two common methods cited above.

INHERENTLY OZONE-RESISTANT ELASTOMERS

A listing of currently available elastomers which have inherent resistance to ozone is provided in Table I. There is nothing in the literature or in our experience to suggest that elastomers in this class are susceptible to attack even at high ozone concentrations. Surface cracks resembling ozone cracking have been observed, upon exposure to ozone, in several of these elastomers, but by use of suitable controls these have been shown to be mechanically induced cracks and not due to ozone. These elastomers are all of the chemically saturated type. Our investigations have indicated that chemical saturation is a necessary, but not sufficient, condition for inherent ozone resistance, since polysulfide rubbers have been shown to crack in ozone at concentrations of 25

and 50 pphm and certain polyurethane rubbers described as "essentially saturated"[9] have also cracked in ozone at similar concentrations. It will be observed that the polymers listed in Table I are of the rarer, specialty type. In those cases in which resistance to very high ozone concentrations over an extended period of time is required, an elastomer from this class should be utilized if possible. Variations in compounding appear to exert little influence on the ozone resistance of polymers in this class, so that little can be said regarding their ozone resistance except that they are completely ozone resistant over a wide concentration of ozone and at various levels of stress.

TABLE II

ELASTOMERS WHOSE DEGREE OF OZONE RESISTANCE IS A FUNCTION OF COMPOUNDING

Chemical name	Trade name or category
Group I.—Chemical Antiozonant Not Required For Ozone Resistance	
Brominated isobutylene-isoprene	Brominated butyl (Hycar 2202)
Isobutylene-isoprene	Butyl (IIR)
Polychloroprene	Neoprene (CR)
Polyurethane	Genthane S
Group II.—Antiozonant Required For Ozone Resistance	
Butadiene-acrylonitrile	Nitrile (NBR)
Butadiene-acrylonitrile-carboxylic acid	Carboxylic elastomer (Hycar 1072)
Butadiene-styrene	SBR
Butadiene-vinyl pyridine	Philprene VP (PBR)
Cis-1,4-polyisoprene	Natural rubber (NR)
Cis-1,4-polyisoprene	"Synthetic" natural rubber (IR)
Cis-polybutadiene	—
Conventional polybutadiene	—
Mercaptan modified adducts of polybutadiene	Chemigum X
Polysulfides	Thiokol
Polyurethanes	Adiprene B, C

ELASTOMERS WHOSE OZONE RESISTANCE IS A FUNCTION OF COMPOUNDING

In Table II, those polymers which yield vulcanizates having varying degrees of ozone resistance are listed. The polymers listed in group I can be compounded, without special inhibitors, to yield vulcanizates which will resist all cracking when exposed to concentrations up to 50 pphm of ozone for very long periods of time at strains up to 30 per cent. Such a degree of ozone resistance cannot be obtained in vulcanizates prepared from polymers listed in group II unless specific ozone inhibitors are utilized. This is the basis on which the division into groups was made. The polymers constituting the bulk of today's rubber consumption are in group II of this table. From a practical standpoint, the ozone resistance of these rubbers *per se* is not as important as the ability to protect them using chemical inhibitors and waxes. Each rubber differs considerably in its response to inhibition against ozone attack. This specificity even extends to rubbers in the same chemical class but differing in monomer ratios or temperature of polymerization[1].

OZONE RESISTANCE OF NEOPRENE (CR) RUBBERS (POLYCHLOROPRENES)

The very good ozone resistance of members of this class of chemically unsaturated polymers is undoubtedly associated with steric hindrance of the

double bonds due to the presence of the halogen; to chemical deactivation of the double bonds; or to a combination of these factors. This ozone resistance varies somewhat depending upon the specific neoprene polymer selected but it has been suggested[10] that this variation may be due to the characteristic lower modulus, in the low strain range, of certain members of this series. Consequently, except for copolymers in which unsaturation is introduced the ozone resistance of this class of materials is not a prime function of the specific polymer selected. Other factors which influence the ozone resistance of neoprene

TABLE III

RANGE OF OZONE RESISTANCE AVAILABLE USING VULCANIZED POLYCHLOROPRENES

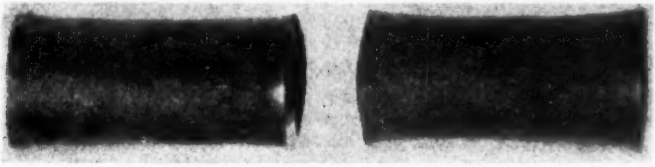
		Appearance under 20 ×magnification	
Polychloroprene	Special additive	Cabinet: ASTM Tentative Method D 1149–55 T[a] Ozone: 25 ±5 pphm, 100 ±2° F Specimen: ASTM Method D 518–44[b] (Method B)	Cabinet: ASTM Tentative Method D 470–56 T[c] Ozone: 10,000–15,000 pphm, Room temperature Specimen: ASTM Method D 518–44[b] (Method B)
Crystallization resistant type	None	No cracks, 18 months	Severe cracks, 1 hr
Crystallization resistant type	None—Specimens air oven aged 70 hr at 212° F	Cracks, 6 hr	Severe cracks, 1 hr
Crystallization resistant type	25 Parts ester plasticizer	Fine cracks, 6 hr	Severe cracks, 1 hr
Crystallization resistant type	5 Parts antiflex-cracking agent 5 Parts PBNA[d] 5 Parts wax	No cracks, 18 months	No cracks, 400 hr
80–20 Blend, polychloroprene plus SBR	15 Parts ester plasticizer	—	Severely cracked, ½ hr
80–20 Blend, polychloroprene plus SBR	15 Parts ester plasticizer plus 4 parts *p,p'*-diamino diphenylmethane	No cracks, 2 yr	No cracks, 550 hr

[a] 1955 Book of ASTM Standards, Part 6, p. 1162. Wherever this designation appears in this paper it refers to a modified cabinet which was enclosed at bottom and provided with forced air circulation through the cabinet at approximately 6 cu ft per min to provide one complete change of air per min. Air flow rate within the cabinet was 1.5 linear ft per sec.
[b] 1955 Book of ASTM Standards, Part 6, p. 1167.
[c] 1955 Book of ASTM Standards, Part 6, p. 1409.
[d] *N*-phenyl-2-naphthylamine.

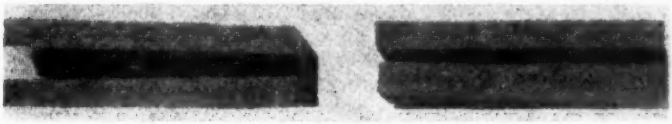
polymers more significantly are (1) the nature and quantity of filler used in the compound[11], (2) the nature and quantity of plasticizers used[12], (3) the quantity and type of antioxidants used[12], and (4) the state of cure and aged condition of the specimens. The data in Table III illustrate the wide range of ozone resistance available using neoprene rubbers. The data presented also illustrate the effect of ozone concentration and compounding variables. The latter effect is especially evident in the case of the ester plasticized 80–20 polychloroprene-SBR blend which was developed for a low-temperature application. The value of using a chemical inhibitor in this compound is very graphically illustrated in Figure 2. It should be emphasized that these results are based on accelerated

tests using relatively high ozone concentrations. Using the information available[10] and ordinary precautions, it is quite possible to develop vulcanizates based on the polychloroprenes which will have excellent resistance to the ozone concentrations experienced in atmospheric exposures in both static and dynamic applications.

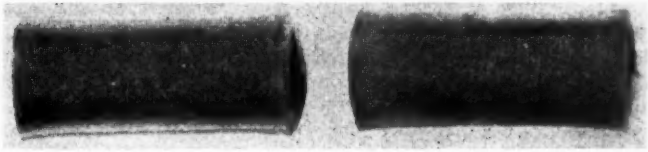
Since the ozone resistance of chloroprene polymers is attributed to their molecular structure, it is difficult to see why the addition of certain non-ozone-sensitive materials, such as plasticizers (or the air oven aging of the specimens) should make the vulcanizates less ozone resistant. This very interesting point is deserving of further investigation.



(*a*) Neoprene vulcanizate, 5 parts anti-flexcracking agent, 5 parts phenyl-2-naphthylamine, 5 parts wax; 400 hr exposure.



(*b*) 80–20, neoprene-SBR blend (no antiozonant); 5 hr exposure.



(*c*) 80–20, neoprene-SBR blend (4 parts *p,p'*-diamino-diphenyl methane added); 550 hr exposure.

FIG. 2.—Exposure of specimens to 10,000–15,000 parts ozone per 10^8 air for periods indicated (ASTM Tentative Method D 470–56 T Apparatus, ASTM Method D 518-44 Specimen).

OZONE RESISTANCE OF BUTYL RUBBER (ISOBUTYLENE–ISOPRENE) AND BROMINATED BUTYL RUBBER VULCANIZATES

The very good ozone resistance of vulcanizates from this class of rubber is due to the low degree of unsaturation present. Blake[13] has reported that a properly vulcanized insulation prepared from a vulcanizate of this class will withstand (bent sharply) a concentration of over 40,000 pphm ozone (0.04 per cent) for an indefinite period of time. Crowdes[14] has indicated that a butyl rubber cable compound has excellent resistance to high ozone concentrations and that (as in the case of neoprene rubbers) oven aging prior to ozone testing reduces the degree of resistance to ozone.

The production of compounds in this class having the high degree of ozone resistance just described is dependent upon proper compounding techniques.

The factors which greatly affect the ozone resistance of butyl rubber[15] are:

1. State of cure—low unsaturation,
2. Polymer grade,
3. Carbon black loading,
4. Plasticizer content,
5. Contamination, and
6. High sulfur.

Of these factors, the state of cure is said to be by far the most important single factor in obtaining maximum ozone resistance from compounds in this class. Both overcures and undercures affect the ozone resistance adversely. Most of the so-called failures noted in the field are traceable directly to undercure[16].

Copolymers of this class are available in several commercial grades depending upon the degree of unsaturation. As might be expected, the best ozone resistance is obtained using those copolymers having the least unsaturation. Closely related to this is the effect produced by contamination of butyl rubber with unsaturated rubbers such as SBR or natural rubber. Even at a level of contamination as low as 0.5 or 1.0 part per hundred parts of rubber, which cannot normally be detected by changes in physical properties, the ozone resistance of the compound is reduced[15]. Insofar as fillers and plasticizers are concerned, low black loadings (of the furnace type) and a minimum of plasticizer should be utilized if the best ozone resistance is desired. Waxes and antiozonants can be used to improve the ozone resistance of these polymers, but they are not essential and it is preferable to compound these polymers for maximum ozone resistance without the use of such additives[16,30]. The ozone resistance of brominated butyl rubber is reported to be similar to that of conventional butyl rubber. In addition, this polymer may be blended with SBR and natural rubber to improve the ozone resistance of the latter two polymers[17].

The study of Lundberg et al.[18], emphasizes that, although highly ozone-resistant compounds can be prepared from the butyl rubber polymers, special attention must be given to proper formulation and compounding.

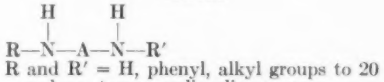
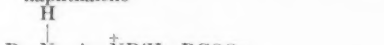
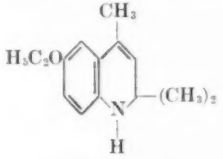
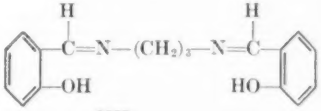
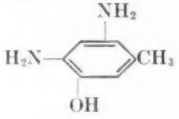
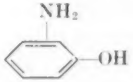
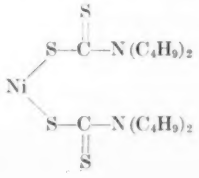
OZONE RESISTANCE OF SBR, NATURAL, AND NITRILE RUBBERS

The problem of ozone cracking is most acute with these rubbers due to their large volume usage and high degree of susceptibility to attack by ozone. Estimations concerning the ozone resistance of vulcanizates based on these polymers, in the absence of specific protectants, vary considerably[19–21]. This is undoubtedly due to the use of different methods of test and to the criteria used in judging the degree of damage. When exposed to ozone at low concentrations and moderate stresses, natural rubber ordinarily develops a multiplicity of fine cracks which tend to stress-relieve the surface thereby moderating further attack. In contrast with this, the SBR and nitrile vulcanizates develop, in most cases, fewer but much larger and deeper cracks. Consequently, an assessment of ozone damage based upon the time of appearance of microscopic cracks might lead in this case to erroneous conclusions in regard to the potential service life of an article. Due to this variation in the nature of damage resulting from ozone attack, unprotected natural rubber is generally considered to have somewhat better ozone resistance than SBR and nitrile rubber. Even less difference has been observed between the resistance of the latter two, with the SBR perhaps slightly better than the nitrile rubber.

To the rubber compounder interested in the preparation of ozone-resistant vulcanizates from these polymers, a more important point of inquiry is the response of these polymers to protection by antiozonants. In this regard, the SBR is much more receptive to protection than either the nitrile or natural rubbers. Of the latter two, the nitrile is more readily inhibited. Numerous

TABLE IV

CHEMICAL TYPES EXHIBITING SPECIFIC ANTIOZONANT POTENTIAL

Chemical name	Structure
Alkyl substituted *p*-phenylenediamines and miscellaneous aromatic amines with structures as indicated	 R and R′ = H, phenyl, alkyl groups to 20 carbon atoms, or alicyclic groups A = One, two, or three aromatic rings either joined or separated by small groups such as CH_2, or condensed systems such as naphthalene
Organic acid salts of alkyl substituted *p*-phenylenediamines	
2,2,4-Trimethyl-6-ethoxy-1,2-dihydroquinoline	
Alkyl substituted *o*-phenylenediamines	
Disalicylalpropylenediamine	
4,6-Diamino-*m*-cresol	
o-Aminophenol	
p-Aminophenol	
Nickel dibutyldithiocarbamate	

tread type SBR compositions have been evaluated (using 3 parts of antiozonant per hundred parts of rubber) which are crack free after exposure in a stressed condition (ASTM Method D 518-44 Method B, Bent Loop) in an accelerated ozone test (ASTM Tentative Method D 1149–55 T, 25 pphm ozone) for periods of over three years and in outdoor exposure at Rock Island, Ill., for over 5 yr.

None of the inhibitors used to produce these results in the SBR will protect either the nitrile or natural rubbers under identical conditions. Using higher inhibitor concentrations (5 parts per hundred parts of rubber), it is possible to protect nitrile rubber for over two years in both accelerated and outdoor tests. Natural rubber is the most difficult of the three to protect. Even at the higher inhibitor level, ozone cracking is observed in accelerated tests after exposure periods of less than one day. The use of even higher than 5 parts per

TABLE V

TIME TO FIRST CRACK (UNDER MAGNIFICATION OF 20 ×) OF OIL PLASTICIZED SBR AND NBR VULCANIZATES

Amount of petroleum oil, parts per hundred parts of rubber	Antiozonant (*N,N'*-dioctyl-*p*-phenylenediamine), parts per hundred parts of rubber	Cabinet: ASTM Tentative Method D 1149-55 T Ozone: 25 ± 5 pphm, 100 ± 2° F Specimen: ASTM Method D 518-44 (Method B)	Outdoors	
			20 per cent elongation	ASTM Method D 518-44 (Bent Loop)
		SBR		
0	3	>28 months	>46 months	>48 months
25	3	Cracked 5 months	Cracked 15 months	>15 months
37.5	3	Cracked 12 days	Cracked 6 months	Cracked 5 months
0	0	2 hr	<1 week	<1 week
		NBR		
0	5	4 months	13 months	>23 months
10 (Saturated type)	5	>8 months	>8 months	>8 months
10 (Naphthenic type)	5	>8 months	>8 months	>8 months
0	0	2 hr	<1 week	<1 week

hundred parts of rubber inhibitor levels will provide better protection. However, in our work 5 parts per hundred parts of rubber has been arbitrarily chosen as the highest practical limit for the following principal reasons:

1. Above this level, pronounced effects on physical properties are observed,
2. Processing properties are adversely affected,
3. Costs become excessive, and
4. Objectionable bloom is sometimes observed.

At stresses of 20 per cent or less, many inhibited natural rubber compounds will maintain a crack-free life in outdoor exposures for periods of over 2 yr. However, increasing the stress to 25 to 30 per cent results in shortening of this crack-free life to 1 yr or less in all cases examined.

Great caution must be exercised in regard to the concentration of antiozonant used. It has been observed in many cases that the use of an amount inadequate for protection is actually worse than use of none at all since an underinhibited vulcanizate when exposed to ozone suffers a few very severe cracks rather than the many fine cracks usually obtained with a completely unprotected vulcanizate.

Of the many chemicals tested as antiozonants, only a comparatively few have exhibited specific activity. These are shown in Table IV. Even among

TABLE VI

INFLUENCE OF ACRYLONITRILE CONTENT ON OZONE RESISTANCE OF NBR VULCANIZATES

Acrylonitrile, per cent	Time to first crack (under magnification of 20×) Cabinet: ASTM Tentative Method D 1149-55 T Ozone: 25±5 pphm, 100±2° F Specimen: ASTM Method D 518-44 (Method B)		Outdoor (loop specimen)	
	No antiozonant	5 parts *N,N'*-dioctyl-*p*-phenylenediamine	No antiozonant	5 parts *N,N'*-dioctyl-*p*-phenylenediamine
0	2 hr	>3 hr	1 day	>4 yr
18	2 hr	>4 months	1 day	>21 months
26	2 hr	1 day	1 week	13 months
35	2 hr	1 day	9 days	2 months
45	6 hr	1 day	2 weeks	2 months

this group most do not afford protection in accelerated ozone exposures. Members from the first class shown have the widest range of application and are most active in combating the effects of ozone.

The degree of protection afforded by these antiozonants is affected by other compounding variables in addition to the base polymer. Among the most important of these are:

1. Amount and type of plasticizer or oil used in the compound,
2. Curing system used,
3. Presence of other age resistors,
4. State of cure, and
5. Type and quantity of filler.

The data in Table V illustrate the effect of petroleum oils on the efficacy of an antiozonant in both SBR and NBR vulcanizates. These data indicate that the effectiveness of this inhibitor is reduced by the presence of large concentrations of oil in the SBR vulcanizates, but the presence of oil does not adversely affect the performance of this inhibitor in NBR vulcanizates. Other similar data have indicated that ester plasticizers such as trioctyl phosphate, even at concentrations as low as 5 parts, interfere seriously with the inhibitor function in SBR vulcanizates. NBR vulcanizates are not affected in this way.

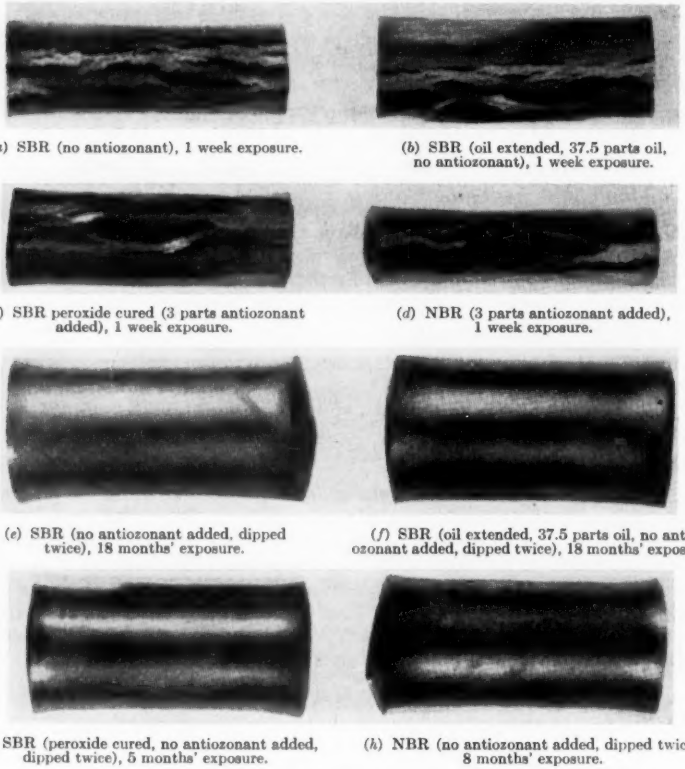
TABLE VII

EFFECT OF CURING SYSTEM ON THE RIME TO FIRST CRACK (UNDER MAGNIFICATION OF 20 ×) OF SBR AND NBR VULCANIZATES

Curing system	Cabinet: ASTM Tentative Method D 1149-55 T Ozone: 25±5 pphm, 100±2° F Specimen: ASTM Method D 518-44 (Method B)		Outdoors, ASTM Method D 518 (Method B)
	Original	Aged 7 days at 158° F	
	SBR[a]		
Sulfur-accelerator	>36 months	2 hr	>48 months
Thiuram-thiazole (Cure No. 1)	>42 months	>40 months	>42 months
Thiuram-thiazole (Cure No. 2)	>28 months	2 hr	>28 months
	NBR[b]		
Sulfur-accelerator	4 months	8 hr	>23 months
Thiuram-thiazole	>16 months	>16 months	>16 months

[a] Contains 3 parts N,N'-dioctyl-*p*-phenylenediamine as antiozonant.
[b] Contains 5 parts N,N'-dioctyl-*p*-phenylenediamine as antiozonant.

It has been reported[22] that a slight increase in resistance to ozone attack was found in the NBR vulcanizates with increase in acrylonitrile content. The data in Table VI would lead to a similar conclusion. However, what is perhaps a more important point is the variation in performance of antiozonant in these vulcanizates as acrylonitrile concentration is increased. It is much more difficult to protect the high acrylonitrile vulcanizates adequately than those



(*a*) SBR (no antiozonant), 1 week exposure.

(*b*) SBR (oil extended, 37.5 parts oil, no antiozonant), 1 week exposure.

(*c*) SBR peroxide cured (3 parts antiozonant added), 1 week exposure.

(*d*) NBR (3 parts antiozonant added), 1 week exposure.

(*e*) SBR (no antiozonant added, dipped twice), 18 months' exposure.

(*f*) SBR (oil extended, 37.5 parts oil, no antiozonant added, dipped twice), 18 months' exposure.

(*g*) SBR (peroxide cured, no antiozonant added, dipped twice), 5 months' exposure.

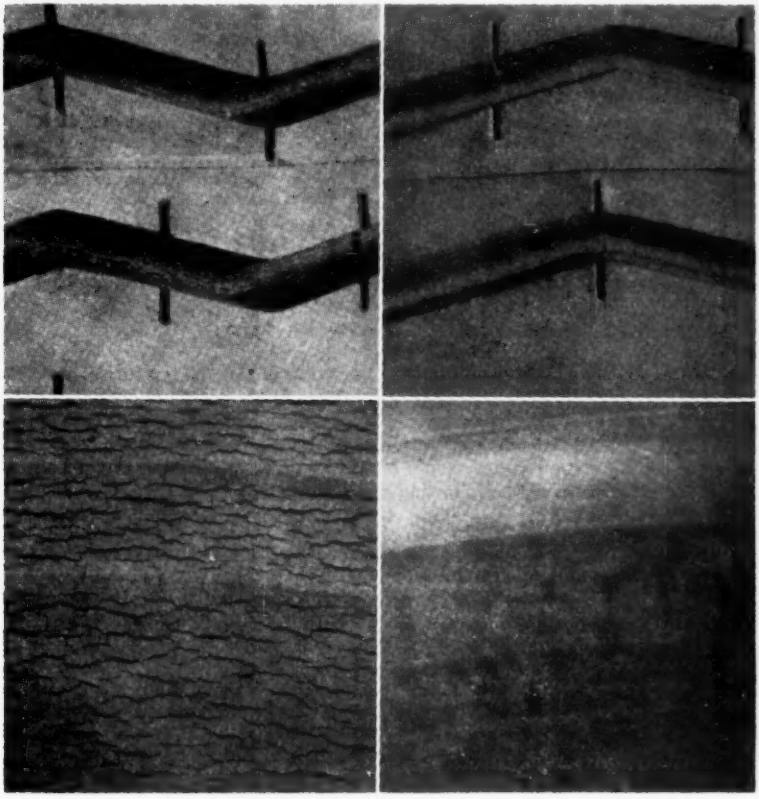
(*h*) NBR (no antiozonant added, dipped twice), 8 months' exposure.

FIG. 3.—Ozone protection afforded vulcanizates by external antiozonant application (ASTM Tentative Method D 1149–51 T, 50±5 pphm O_3 at 100±2° F).

having the lower acrylonitrile content. A related case is that of SBR-NBR blends in which it is found that under comparable conditions of inhibition and cure the antiozonant does not exhibit satisfactory inhibition against ozone cracking until over 50 per cent of the polymer is SBR.

In Table VII are presented data which show the influence of curing system on the ozone resistance of inhibited SBR and NBR vulcanizates. The nonsulfur curing systems, long recognized as having superior shelf age resistance over sulfur-based cures, respond more satisfactorily to inhibition against ozone cracking. Very little difference is observed in accelerated tests between the

ozone resistance of sulfur-cured and non-sulfur-cured compounds when they are uninhibited. The retention of ozone resistance in several of these vulcanizates after oven aging is especially noteworthy since it indicates that factors other than volatilization and deactivation of the inhibitor may be responsible for the frequently observed loss of ozone protection after oven aging of the vulcanizates.



(*a*) Uncoated. (*b*) Brush coated twice.

FIG. 4.—Ozone protection afforded a tire by external antiozonant application. Tire exposed 18 months on roof at Rock Island, Ill.

Other curing systems such as the dicumyl peroxide are completely incompatible with amine type antiozonants[23]. Due to an apparent reaction between the peroxide and the amine inhibitor, compounds prepared using this combination do not cure properly. However, it is possible to protect peroxide-cured vulcanizates and also vulcanizates based on the usual curing systems (which have not been especially inhibited against ozone attack) by application of an antiozonant solution on the surface of the cured article. The preferred tech-

TABLE VIII

TIME TO FIRST CRACK (UNDER MAGNIFICATION OF 20 ×) UNDER ACCELERATED AND OUTDOOR DYNAMIC EXPOSURE CONDITIONS

Type of ozone inhibition	Type of rubber	Firestone weathering apparatus 15±5 pphm ozone at 100±2° F	Outdoor flexing (O-ring specimens)
None	SBR	2 hr	1 day
Dipped twice in 50–50 antiozonant[a]-acetone solution	SBR	150 hr	90 days
3 parts antiozonant[a] incorporated at time of mixing	SBR	36 hr	18 days
None	NBR	2 hr	Data not available
Dipped twice in 50–50 antiozonant[a]-acetone solution	NBR	15 hr	Data not available
5 parts antiozonant[a] incorporated at time of mixing	NBR	12 hr	Data not available
None	Natural rubber	2 hr	Data not available
Dipped four times in 50–50 antiozonant[a]-acetone solution	Natural rubber	>187 hr	Data not available
5 parts antiozonant[a] incorporated at time of mixing	Natural rubber	4 hr	Data not available

[a] N,N′-dioctyl-*p*-phenylenediamine.

nique is to apply by brushing or dipping two coats of a 50–50 mixture of dioctyl-*p*-phenylene diamine and acetone to the surface of the article allowing approximately 4 hr drying time between coats. Using this method, it is possible to obtain protection (no cracking observable under magnification of 20×) in accelerated (25 and 50 pphm ozone) and outdoor tests for extended periods of time for vulcanizates of the following descriptions:

1. Sulfur-accelerator cured SBR,
2. Oil extended and plasticized sulfur-accelerator cured SBR,
3. Peroxide cured (dicumyl peroxide) SBR,
4. SBR vulcanizates which have been air oven aged for 70 hr at 212° F (prior to exposure to ozone atmosphere but after application of inhibitor),
5. NBR vulcanizates, and
6. Natural rubber vulcanizates (3 to 4 coats required).

Examples of the protection available in accelerated ozone exposures by use of this method are shown in Figure 3. Outdoor exposures have been conducted concurrently on similar specimens with equally satisfactory results. This technique should be especially applicable to the large volume of rubber goods in storage which has not been specifically inhibited against ozone cracking. An example of the application to such an item is shown in Figure 4. As may be seen, the coated areas of the tires of crack-free after 18 months outdoor exposure. Cracking was observed in the untreated areas after 5 days exposure and became progressively worse as indicated in Figure 4. The data in Table VIII illustrate the degree of protection obtainable in dynamic ozone testing. The Firestone weathering apparatus[24] applies a cyclic stress (60 cpm) of 0 to 20 per cent elongation while the specimen (1 in. by 6 in. by 0.075 in.) is rotated through 360 deg in a cabinet having a regulated ozone concentration. In the Rock Island Arsenal outdoor flexing apparatus[1] O-ring specimens ($\frac{1}{4}$ in by 6.5 in outside diameter) are alternately stretched and relaxed (0 to 25 per cent

elongation) at the rate of 4 cpm. As the data indicate, a considerable improvement in ozone resistance is obtained when the antiozonant is applied topically compared to either the uninhibited vulcanizates or those vulcanizates containing up to 5 parts antiozonant incorporated into the compound prior to cure.

Studies using a radioactively tagged antiozonant and a radioautographic technique have indicated that the antiozonant when externally applied does not migrate throughout the bulk of the rubber. The antiozonant does penetrate sufficiently to become an integral part of the rubber so that visually it is difficult to distinguish a coated from an uncoated specimen. The prevention of

TABLE IX

OZONE RESISTANCE OF MISCELLANEOUS ELASTOMERS

		Time to first crack		
		Cabinet: ASTM Tentative Method D 1149–55 T, 100±2° F Specimen: ASTM Method D 518–44 (Method B)		Outdoors Specimen: ASTM Method D 518–44 (Method B)
Elastomer	Antiozonant	25±5 pphm ozone	50±5 pphm ozone	
Carboxylic	None	1 day	6 hr	13 weeks
Carboxylic	3 parts N-phenyl-N′-cyclohexyl-*p*-phenylene-diamine	>1 yr	>1 yr	>1 yr
Carboxylic	3 parts N,N′-di-octyl-*p*-phenylenediamine	3 days	1 day	11 months
Polyurethane No. 1	None	8 days	7 days	>2 weeks
Polyurethane No. 2	None	4 days	—	>2 weeks
Polyurethane No. 3	None	>30 days	>30 days	>1 month
Quaternized butadiene-methyl vinyl pyridine	None	hr	2 hr	1 day
Quaternized butadiene-methyl vinyl pyridine	3 parts N,N′-di-octyl-*p*-phenylenediamine	8 hr	6 hr	1 week
Quaternized butadiene-methyl vinyl pyridine	3 parts nickel dibutyl dithiocarbamate	8 hr	6 hr	>1 yr
	3 parts disalicylal-propylenediamine	8 hr	6 hr	>8 months
Polysulfide No. 1	None	1 day	6 hr	—
Polysulfide No. 2	None	1 day	6 hr	—
Cis-1,4-poly-isoprene	None	2 hr	2 hr	4 days
Cis,4-poly-isoprene	5 parts N,N′-dioctyl-*p*-phenylenediamine	4 hr	4 hr	>1 month
Cis-polybuta-diene	None	2 hr	2 hr	6 days
Cis-polybuta-diene	3 parts N,N′-dioctyl-*p*-phenylenediamine	4 hr	2 hr	>1 month

ozone cracking using this technique leads one to believe that the mechanism by which antiozonants serve to protect rubbers is a combination of physical and chemical processes. Most of the known facts may be reconciled with a mechanism of protection consisting of the reaction of ozone (and oxygen) with the diamine at the surface of the rubber to form an ozone inert surface which has sufficient flexibility to be able to withstand most of the stresses imposed upon the specimens.

OZONE RESISTANCE OF MISCELLANEOUS ELASTOMERS

The results of ozone exposure tests made on several elastomers, from the group whose ozone resistance is dependent on compounding, are shown in Table IX.

The carboxylic rubber[25] is slightly more ozone resistant, in the absence of antiozonants than the closely related nitrile rubber vulcanizates. It responds satisfactorily, but with an extremely marked specificity, to inhibition against ozone cracking. Ester plasticizers interfere with the protective action of the antiozonant.

The polyurethane elastomers exhibit a wide range of ozone resistance depending, no doubt, upon their chemical makeup. As might be expected, those containing the highest amount of unsaturation have the poorest ozone resistance. No information could be found on the effect of antiozonants in these polymers. External antiozonant application has been found to improve greatly the ozone resistance of these polymers. At least one of the available types appears to be sufficiently ozone resistant to meet all service requirements in outdoor exposures[26].

The quaternized butadiene-methyl vinyl pyridine copolymers[27] are about as susceptible to ozone cracking as the SBR and nitrile rubbers. However, they are not nearly as responsive to inhibition as the latter rubbers. None of the phenylenediamine antiozonants will protect this copolymer during accelerated ozone exposures. This has been shown[28] to be due to a reaction between the amine antiozonant and the organic halide used as the quaternizing agent.

A new family of elastomers, members of which are reported to have excellent resistance to ozone, has recently been described[29]. These are the mercaptan adducts of butadiene rubbers. It is claimed that the 95 per cent saturated methyl mercaptan-butadiene rubber adduct suffers no cracking after exposure in a stressed condition to ozone concentrations of 2750 $\pm$ 5 pphm for 24 hr and to 50 pphm for over 200 hr. Dynamic ozone resistance is also reported as excellent.

In view of their chemical saturation and generally recognized resistance to ozone cracking in outdoor exposures, the results of accelerated tests showing early cracking in the polysulfide rubbers were indeed surprising. It is believed that the ozone attacks sulfur atoms in the main chains, producing scissions which result in cracking indistinguishable from the cracks resulting when double bonds in the main chains of the unsaturated rubbers are ruptured.

Tires based on *cis*-1, 4-polyisoprene (synthetic "natural" rubber) have been reported[31] to have better crack resistance than tires based on natural rubber, although ozone cracking is not specifically mentioned. Our results indicate that the ozone resistance of this polymer in the absence of antiozonants closely resembles that of natural rubber. Its poor response to inhibition against ozone cracking using antiozonants also closely parallels results obtained with natural rubber.

The ozone resistance of vulcanizates (containing no antiozonant) based on *cis*-polybutadiene is similar to that of vulcanizates based on conventional polybutadienes. However, vulcanizates based on the *cis*-polybutadiene are not readily protected by antiozonants. This is in marked contrast to the conventional polybutadienes which are readily protected against ozone cracking by suitable inhibitors. It appears, therefore, that the stereochemical configuration of the polymer does not affect its inherent ozone resistance but does affect the readiness with which the polymer can be protected by antiozonants.

SUMMARY

This review has attempted to categorize and describe the degree of ozone resistance available both within and among the various elastomers.

Some of the factors affecting ozone resistance and means for obtaining ozone-resistant vulcanizates have been discussed.

It has been indicated that by judicious selection of elastomer and compounding ingredients, resistance to very severe ozone conditions may be obtained with the currently available elastomers.

The dependence of ozone resistance on proper compounding of the ozone susceptible rubbers has been emphasized. This has led to the conclusion that certain rubbers considered to be ozone resistant behave in the expected manner only if proper attention is given to compounding variables.

ACKNOWLEDGMENT

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OZONE RESISTANCE OF RUBBER INSULATIONS *

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INTRODUCTION

The insulation of high voltage cables is protected from corona by the application of electrical shields of semiconducting materials or metallic tapes. Accidents in installation may result in the exposure of small areas of the insulation to corona by the creation of gaps in or under the protective shields. Long experience has shown that while the electrical shielding is essential at voltages above 2000 to 5000, it cannot be depended on completely to eliminate corona and the accompanying high concentrations of ozone. Therefore it is necessary to make compounds intended for use as high voltage insulation resistant to ozone cutting. There are several important features of high voltage service that determine the avenues open to the compounder in developing a high voltage rubber insulation. For the most part, high voltage cables are permanently installed and are not subject to movement after being energized. Since high voltage cables are permanently installed, dynamic properties of the insulation are not important, and the conditions under which ozone resistance must be maintained are correspondingly less demanding. Of course, the probability of some exposure to high voltage corona makes necessary resistance to concentrations of up to 0.2% ozone under these static conditions. High voltage insulation is applied in heavy walls and is protected by semiconducting and metallic tapes, so that the requirements for tensile strength, ultimate elongation, modulus, abrasion resistance and compression set are not very demanding. This provides still more latitude for the compounder and this latitude is very necessary. The makers and users of high voltage cable recognize that stresses in the insulation and wrinkles in the shielding tapes which may result from bending the cables too sharply during installation will be very likely to create conditions that not only permit corona to develop but also promote cutting of the insulation. Standards have been established governing the minimum bending diameters for cables during installation, but these standards are not always followed and provision must be made for the cable to operate successfully in spite of having been bent too sharply.

High voltage insulations which meet these conditions successfully have been made from natural rubber or SBR in spite of the low inherent resistance to ozone of these polymers. Success has been achieved with these materials by heating the installed cables before energizing or by the use of bitumens or factice in the compound to accelerate the rate of stress decay[1].

EXPERIMENTAL

Early in the course of this investigation the importance of the role of stress decay was established. SBR compounds of the type similar to A in Table I

* An original contribution. Presented at the Los Angeles meeting of the Division of Rubber Chemistry, ACS, May 14, 1959.

TABLE I

Compound	A	B	C	D	E
Natural rubber		100			
SBR	100				
Butyl rubber (150)			100	100	100
Factice, bitumen or the like		100		30	
Gilsonite	60	100			37
Zinc oxide	5	13	5	7	5
Solid fillers		33	80	150	90
Waxes	9	26	8	16	14
Antioxidants	1.0	1.25			
Accelerators	1.5	1.25		5	4.2
Sulfur	2.4	1.4			0.9
Quinone dioxime or derivatives			6	2.5	
Red lead			10	1.3	

were found to have outstandingly good electrical strength, but normally very poor performance in the accelerated test for corona resistance known as the "Vertical U" test. In this test, a sample of insulated wire is bent around a mandrel so that the bending diameter is a multiple of the diameter of the insulated wire smaller than the minimum specified for installation. The bend chosen for the test is severe, for example, in this paper wires whose specified minimum bending diameter is 8.0 times the wire diameter are bent at $2\frac{1}{2}$ times wire diameter. Therefore the stresses in the surface of the test samples are much higher than those permitted in installation. This testpiece, usually with the ends fastened together so that the sample appears U shaped, is place with the bottom of the bend on a grounded metal plate and a voltage giving a stress of 100 or 125 volts per mil of insulation is applied between the conductor and the plate (Figure 1). Active corona appears between the insulation and the plate near the point of contact with the plate. As shown in Figure 2 samples of Compound A fail on the Vertical U test after rest periods (after bending) of up to 2112 hours at 76° F. Samples which were held in an oven at 106° F for as

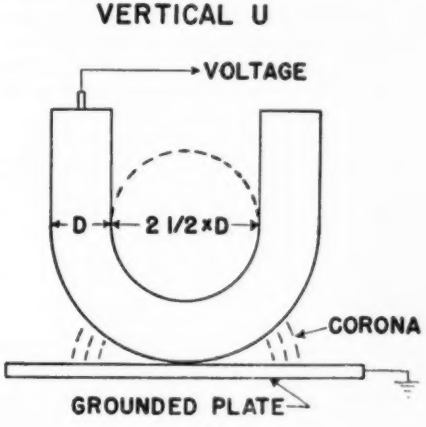

FIG. 1.

Relaxation at 76° F

Hours Rest	Min. to Fail ("Vertical U")
264	13
507	10
1085	9
2112	18

FIG. 2.

little as 2 to 3 hours after bending, however, passed the Vertical U test as shown in Figure 3. The results shown in Figures 2 and 3 underline the critical role of stress relaxation in the resistance of rubber insulation to corona. Compound A, which obviously is inherently vulnerable to corona, cutting badly in 10 to 20 minutes even after long rest periods at 76° F becomes extremely resistant to cutting in corona after short rest periods at 106° F. The difference is attributed to rapid stress decay at the higher temperature. The important factors are relaxation time and temperature, and in the case of a compound like A, the temperature of relaxation is obviously very important. Compound B (Table I) is an example of a high voltage insulation based on natural rubber, formulated similarly to Compound A except that it is designed for rapid stress decay at normal temperatures. This compound is resistant to corona.

Butyl rubber because of its relatively low unsaturation is potentially much more resistant to the chemical action of ozone and corona than natural rubber or SBR. It is also very free from nonhydrocarbon constituents and therefore ideal as the base polymer for electrical insulation with high resistivity, low dielectric constant and power factor and the ability to maintain stability of these properties during exposure to moisture. It is not surprising that from the time of its first appearance on the market it has been of great interest to the makers of insulated wire, particularly for high voltage application. Com-

Relaxation at 106° F

Hours Rest	Min. to Fail ("Vertical U")
0.5	5
2.1	480
2.8	>24,000

FIG. 3.

pounds C, D and E in Table I represent different approaches to the problem of preparing a satisfactory high voltage insulation based on butyl rubber.

Compound E derives from the natural rubber and SBR compounds in the table, except that unlike Compound B it does not contain materials promoting rapid stress relaxation. Compound E has an excellent balance of physical and electrical properties, and thanks to the low unsaturation of butyl rubber it ages very well and its resistance 0.04% ozone is excellent. Unfortunately it fails very rapidly in the Vertical U test regardless of rest at room temperature after the sample is bent. It will presently be shown that this compound is much more resistant to ozone than Compound B, yet the latter passes the Vertical U test, which indicates that it should be satisfactory for service as high voltage insulation, while Compound E fails this test and is unsatisfactory for high voltage service. On the basis of the performance of Compound A it was judged that Compound E must be cutting in corona because its rate of stress relaxation is too low.

The same disappointments were encountered in the case of Compound C. Here the formulation is based on a nonsulfur cure of the butyl rubber which results in outstanding aging resistance. It was suggested that since a very high state of cure is reached with the quinone dioxime types of vulcanizing agents, the residual unsaturation of the vulcanizate would be lower and the resultant chemical resistance to ozone greater[2]. As will be seen later, this is true. However, Compound C, although in every other way an acceptable high voltage cable insulation, fails the Vertical U test after short exposures and regardless of rest periods allowed after formation of the U shaped testpiece.

At this point it becomes apparent that a new approach is needed in developing high voltage rubber insulations. Two otherwise promising compounds, which ought to have outstanding resistance to cutting in corona (or ozone), have failed to meet just this requirement. The evidence of time consuming measurements of the effect of rest periods after the Vertical U test samples are bent indicate that this is a significant factor. A way is needed to develop such answers more quickly and conveniently.

The corona resistance of rubber high voltage cable insulations may be considered to have two components which are independent of each other. The first is ozone resistance measured in such a way as to be unaffected by stress decay, and the second is the rate of stress decay at normal temperatures. The resistance of a vulcanizate to ozone under a constant load is independent of the rate of stress decay and it may be measured very readily by suspending in the ozone chamber tensile testpieces supporting selected weights. Samples of a given compound will fail in longer or shorter times depending upon the initial load. Failure is taken as the time for the sample to break, and this differs very little from the time for the first appearance of visible cracks, since the rate of cut growth is very high under load. This endpoint is definite and not subject to observational errors. The results of many tests indicate that the log of the time to failure is inversely proportional to the log of the initial tension, a result which has also been obtained by Zuev[3].

Results for several compounds are shown in Figure 4. Note that when measured in this way the ozone resistance of the natural rubber Compound B is very much less—that is cutting occurs at shorter times and at lower tensions—than the ozone resistance of the butyl Compounds E and C. This result is to be expected, because of the higher unsaturation of the base polymer. The ozone resistance of the butyl compound vulcanized with sulfur is less than that of the quinone dioxime type vulcanizates C and D, as would be predicted from

the higher state of vulcanization attained with these nonsulfur vulcanizing agents. It should also be repeated that the natural rubber compound showing here low ozone resistance at constant load consistently passes the Vertical U test, in contrast with the more highly ozone-resistant compounds C and E, which consistently fail on the Vertical U test. As will be shown, the 0.2% ozone concentration selected for the tests, the results of which are given in Figure 4, gives good agreement with the Vertical U test.

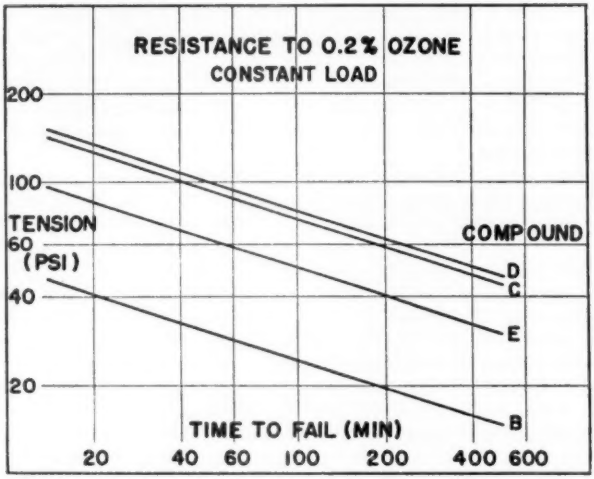

FIG. 4.

It is interesting that all the lines for ozone resistance at constant load are roughly parallel on the log-log plot. Reduced to empirical equations relating initial tension with time to fail:

$$(\text{Tension-psi})\,(\text{time-minutes})^a = b$$

For Compound B, a is equal to 0.30 and b is equal to 102. In the case of Compound D, having the highest ozone resistance at constant load, a is equal to 0.328 and b is equal to 357. There is reason to believe that the form of this equation should be—

$$(\text{Tension-}T_c)\,(\text{time})^a = b$$

where T_c is a critical tension below which cutting does not occur. The data available are not accurate enough to permit a reliable estimate of this critical tension to be made. It would be very interesting to try to determine this critical tension, because it should be sensitive to changes in the degree of unsaturation in the polymer, protection of the double bond by an adjacent chlorine atom and other structural variations. A carefully controlled study of ozone cutting under constant load should be a useful tool in the investigation of the mechanism of ozone cutting.

The second criterion for corona resistance, stress relaxation at constant strain, may easily be measured. The use of a flat spring and strain gauge makes

possible very sensitive measurements of stress. A tensile specimen is gauge marked and attached to the free end of the flat spring. It is then rapidly extended to a predetermined elongation by means of a screw. The stress is read at intervals and during the early part of the test when relaxation is rapid the elongation is maintained at a constant value by slacking off on the screw. After a brief transition period at the start of the test a plot of stress against the log of time is linear. The factors of interest in a stress versus time plot are the magnitude of the stress retained at any time, and the slope or rate of stress relaxation. In studying practical compounds containing various fillers and softeners it appears that the rate of stress relaxation is the ruling variable, since there is certainly a minimum acceptable value of modulus (measured at 20

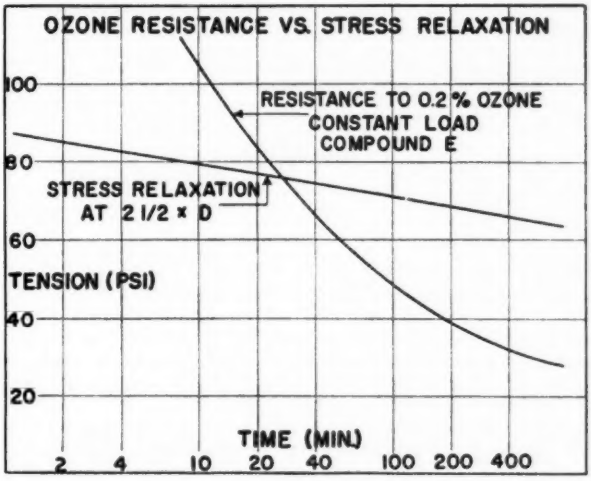

FIG. 5.

inches per minute). That is, unlimited amounts of plasticizer cannot be used because of minimum modulus or hardness requirements, therefore plasticizers giving the highest rates of stress decay when used in tolerable quantities must be sought.

In Figure 5 a portion of the stress relaxation curve for Compound E is shown. Tension is plotted against the log of time. In the same figure is a curve for time to fail at constant load in 0.2% ozone for the same compound. In this case the stress relaxation was measured at 25% elongation, which corresponds to the extension caused on the surface of insulation when a piece of insulated wire is bent around a mandrel having $2\frac{1}{2}$ times the diameter of the wire. This is equivalent to a very severe Vertical U test. The curves in Figure 5 show that even after long rest periods at room temperature enough stress remains in the outer layers of insulation E bent at this curvature to cause rapid cutting. For example, after 10 hours relaxation the resultant stress is sufficient to cause cutting in less than an hour. As mentioned previously, this insulation consistently fails to pass the Vertical U test.

Figure 6 shows curves for ozone resistance at constant load and stress re-

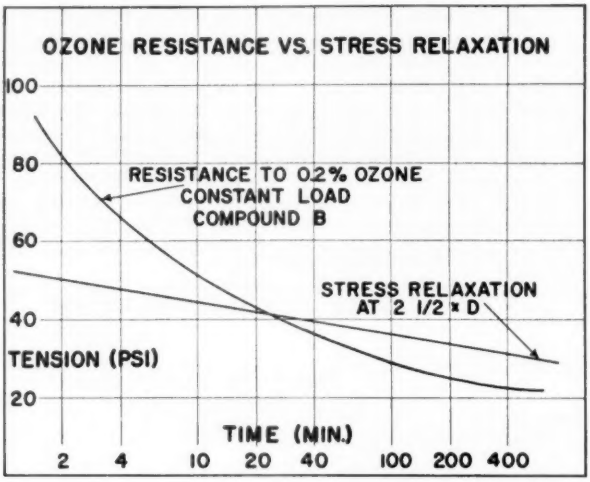

FIG. 6.

laxation measured on Compound B, the insulation containing natural rubber. The ozone resistance curve is of course much lower on this diagram than the ozone resistance curve for the previous Compound E, because Compound B cuts rapidly at lower tensions. However, the modulus at an elongation corresponding to a $2\frac{1}{2}$ times diameter bend for this compound is much lower than that of Compound E and the rate of stress relaxation is greater percentagewise.

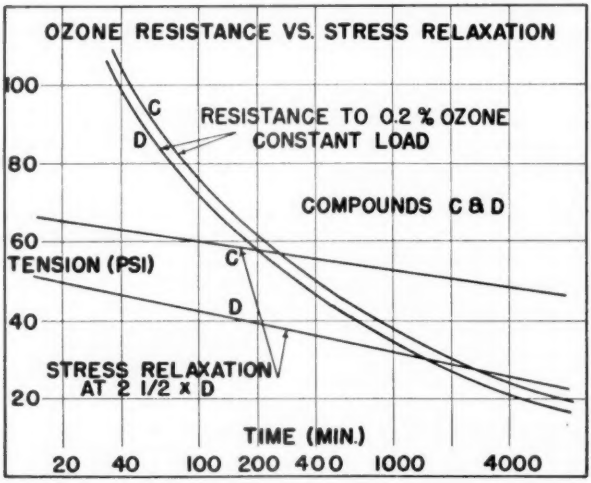

FIG. 7.

The two curves intersect after about the same time interval, but the stress relaxation curve for the natural rubber lies much closer to the ozone resistance curve and the slopes of the two curves become equal at about 300 minutes. Allowing for the possible errors in determining the position of these two curves, it appears that with a suitable rest period this insulation may withstand corona. As will presently be shown, it does successfully pass the Vertical U test after a short rest.

In order to contrast the pair of curves for a compound which pases the Vertical U test with those for a compound which does not, curves for Compounds C and D are shown together in Figure 7. The ozone resistance at constant load of these two compounds is almost identical. The significant difference between the two compounds is shown in the stress relaxation curves. Compound C has a higher initial tension and a lower rate of stress decay than D, and in fact insulation made with Compound C will always cut in the Vertical U test in spite of extremely long rest periods after bending, while short rest periods are sufficient to permit Compound D to pass the test.

TABLE II

EFFECTS OF STRESS RELAXATION ON VERTICAL U RESULTS

Rest temp. °F / Compound	Time in hours: 80 Rest to fail		106 Rest to fail		158 Rest to fail	
A	191	0.1	2.1	8.0	0.2	>23
			2.8	408		
B	0.1	>67				
C			504	0.7	739	1.3
D	0.1	8.7				
	0.3	>23.6				

The choice of a plasticizer which permits a sufficiently rapid stress relaxation without lowering excessively the modulus of the compound is the margin between success and failure in resisting exposure to corona, as demonstrated by this pair of compounds.

Table II summarizes the results of an extensive study of the effect of rest at various temperatures after bending on the behavior of insulation exposed to corona. Compound A is shown to be very sensitive to the rest temperature. At 80° F even long rest periods do not increase time to failure on the Vertical U test. At 106° F a few hours relaxation is enough to allow samples to pass the test, and at 158° F a few minutes rest is ample. Of course a compound with these characteristics could be used for high voltage insulation if the installed cable were heated to 158° F before being energized. This would relax the stresses created by bending the cable during installation, and even at the few points where corona might exist the relaxed insulation would not cut. As a practical matter neither the makers nor the users of high voltage cable would care to be dependent on this expedient. The natural rubber Compound B which has very low ozone resistance at constant load, but which relaxes rapidly as shown in Figure 6, passes the Vertical U test after only a few minutes rest at room temperature. There can be no question but that relaxation of stress in the surface of the bent sample is responsible for the good performance of this compound, in view of its very low resistance to cutting in ozone under constant load. By way of contrast Compound C, which has been shown to have very high resistance to ozone cutting under constant load and high modulus at 25%

elongation together with a low rate of stress relaxation, fails quickly in corona. Long rest periods at elevated temperatures do not impart corona resistance to this compound. With the addition of a suitable softener to permit rapid stress decay Compound D, otherwise very similar to C, easily passes the Vertical U test after 15 to 20 minutes rest at room temperature, although 5 to 10 minutes rest is not sufficient.

These results may be summarized as follows: High voltage insulation can be expected to withstand ozone or corona if the initial modulus at 50% elongation is low and if stress relaxation proceeds rapidly enough so that stresses sufficient

TABLE III

EFFECTS OF STRESS RELAXATION VERTICAL U VS. OZONE

Compound	Relaxation temp. °F	Vertical U Hours relaxation required to pass 20 Hour test	0.2% ozone Hours relaxation required to pass 3 Hour test
A	106	50	20
	158	0.17	0.17
B	RT	0.1	0.1
C	158	>2688	>96
D	RT	0.3	0.1

to cause failure do not long remain in the surface of bent samples. Vulcanizates having very high ozone resistance at constant load can tolerate higher stresses than vulcanizates having lower ozone resistance, but unless stress relaxation results in a gradual reduction of such stesses, eventually failures will occur.

The use of an ozone chamber is necessary to measure ozone resistance at constant load. Tables III and IV give results of Vertical U and ozone chamber tests which indicate that 0.2 per cent ozone is a concentration producing results comparable to those which are obtained in the corona test. A direct comparison of the rest periods required to resist corona or ozone cutting is given for each

TABLE IV

OZONE RESISTANCE IMMEDIATE EXPOSURE 2 × D

Compound	C	D
0.06% Ozone	>8 Hours No cuts	>8 Hours No cuts
0.20% Ozone	1.25 Hours Failed	>6 Hours No cuts
0.55–0.65% Ozone	0.42 Hours Failed	1.0 Hour Failed

of four different insulations. In both exposures the samples were bent to the same diameter and then allowed to relax under the conditions described. It should be remarked here that the ozone test is restricted to 3 hours as a matter of practical operations. At 0.2% ozone concentration bent samples which pass the 3 hour test will usually last for many more hours. Samples which fail usually fail in a matter of minutes. Therefore it is considered satisfactory to compare the shorter test in 0.2% ozone with the 20 hour Vertical U test which is allowed to run overnight. Compounds based on NR, SBR and butyl all are found to perform similarly in the two tests, and considering the variance of each method of testing, the close agreement is surprising. Although the rest

periods required to enable bent samples to resist 0.2% ozone or corona are very nearly equal, the rate of cutting in 0.2% ozone is slightly slower than that in the corona. A comparison of the results in Table IV with those in Table II shows that Compound C cuts in 0.7 to 1.3 hours in corona after long rest periods and cuts in 0.2% ozone in 1.25 hours when exposed immediately after bending. Compound D cuts in 8.7 hours when exposed to corona after 5 minutes rest and is still not cut after 6 hours in 0.2% ozone, exposed immediately after bending. The difference in the rates of cutting is small, but the corona is apparently slightly more severe than 0.2% ozone. Results for exposure to 0.55 to 0.65% ozone are also shown in Table IV. Difficulty was experienced in holding the high concentration, and therefore the upper and lower limits of the ozone con-

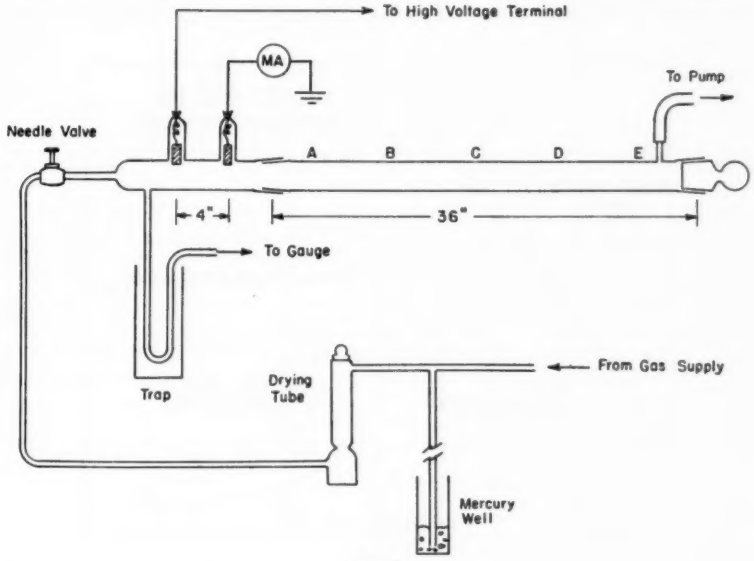

FIG. 8.

centrations used in this test are shown. In 0.55 to 0.65% ozone bent samples cut more rapidly than they do in corona. Compound D, which lasted 8.7 hours before failing on the Vertical U test, is badly cut in 1.0 hour. As the result of these comparisons 0.2% ozone is taken as a concentration correlating well with the results of test in corona discharge, and it was on this basis that it was used for many of the tests reported here.

In the course of studying ozone and corona resistance, the question was raised as to the nature of the active agent in corona which casues cutting of stretched rubber insulation. It is known that ozone is present in corona, but is ozone the only active agent or may atomic ozygen be present? A study of the literature revealed that atomic oxygen is produced in the range of 1 mm Hg pressure[4] and it seemed possible that some might be created momentarily in the high intensity discharge at the surface of the rubber during a Vertical U test, and that this might influence the test results. It was decided to test this

hypothesis by studying the cutting of vulcanizates at various pressures in a small chamber immediately adjacent to an electrical discharge[5]. The apparatus for this test is shown in Figure 8. Provisions were made for supplying dry air or other gases and the samples could be positioned near, or at some distance from the discharge. Initial experiments were carried out in dry air and as the pressure was lowered some very interesting discoveries were made.

As the pressure decreases from 10 mm of mercury, the rate of cutting of butyl rubber compounds increases very rapidly, while the rate of cutting of vulcanizates of NR or SBR decreases rapidly (Figure 9). The insertion of a glass wool plug between the samples and the source of discharge increases the rate of cutting of NR and SBR compounds. The increase in the rate of cutting of the butyl vulcanizates while the rate of cutting of SBR and NR is decreasing is interpreted as evidence of the presence of atomic oxygen, generated in the dis-

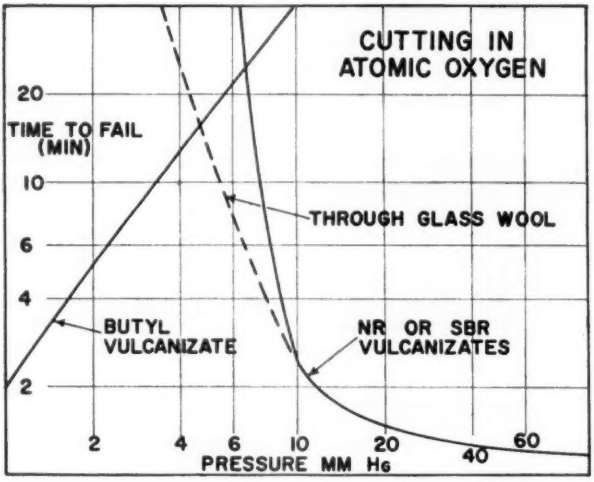

FIG. 9.

charge, and stable in this pressure range. Butyl rubber may be expected to cut in atomic oxygen because of the tertiary carbon atom in the chain, while apparently the double bonds in NR and SBR are not attacked by atomic oxygen, at least not in such a way as to cause chain scission. When the glass wool plug is placed between the discharge and the stretched samples, some atomic oxygen recombines with the formation of a higher proportion of ozone which causes more rapid cutting of the NR and SBR testpieces.

Table V shows the results of attempts to reduce the rate of cutting butyl rubber vulcanizates in atomic oxygen by varying the polymer or by adding various antioxidants. No significant change resulted from any of these modifications. Neither the very low unsaturation of R-2 butyl nor the higher unsaturation of the GR-I 25 produced much change in the rate of cutting. The slightly slower rate of cutting of the R-2 vulcanizate may well result from the lower modulus and consequent lower stress in this bent sample. The addition

of four different antioxidants produced no measurable difference in the rate of cutting.

Surface coatings have been used successfully to protect against ozone and it was found that surface coating will also protect against atomic oxygen. Table VI gives results for butyl vulcanizates protected by an ozone-resistant lacquer and by a layer of natural rubber latex. Both of these coatings were effective in increasing the resistance of butyl rubber vulcanizates to atomic oxygen. Also shown in Table VI are the results of tests on neoprene and Hypalon which

TABLE V

CUTTING IN ATOMIC OXYGEN BENT SAMPLES—1 MM HG PRESS

Type of butyl	Antioxidant	Minutes to cut
R-2	None	10*
25	None	8
50	None	8
50	DBNPPD	8
50	PBNA	8
50	DPPD	8
50	DHTMQ	8

* Low modulus.

show considerable resistance to atomic oxygen. These materials and the lacquer coated sample are of particular interest because they are resistant to both ozone and atomic oxygen. Therefore, they could be used in missiles where corona resistance might be required at both atmospheric and at very low pressures.

The results of this investigation of cutting at very low pressure indicate that atomic oxygen cannot be present in significant amounts in corona discharges at atomospheric pressure, since it is a powerful cutting agent for those

TABLE VI

CUTTING IN ATOMIC OXYGEN

Vulcanizate	Surface coating	Minutes to cut
Butyl	None	8 to 15
Butyl	Lacquer	>300
Butyl	Latex (NR)	>280
Neoprene	None	300
Neoprene (ozone resistant)	None	>350
Hypalon	None	350

(Bent samples at 1 mm Hg)

butyl rubber vulcanizates that have been found to resist corona at atmospheric pressure very well.

CONCLUSIONS

It has been shown that the resistance of high voltage rubber insulation to corona is dependent not only upon the ability of the compound to resist cutting at constant load but also upon its rate of tensile stress decay at constant elongation. These two properties of a vulcanizate can be studied independently and the information obtained in this way may be applied to the development of improved corona-resistant compounds. In the process of developing new compounds or improving the performance of old ones changes may be made in

curing ingredients, fillers, or softeners. Any one of these changes can affect both the ozone resistance at constant load and the rate of stress relaxation. When tests are made on bent samples in ozone or corona the changes in both properties may well be confounded so that the compounder does not know which one has been changed decisively. For example, the addition of a softener which increases the rate of stress relaxation may adversely affect the resistance to ozone at constant load. On the other hand, it may be that the plasticizer simply does not lower the modulus or increase the rate of stress decay enough. It is important to know whether it is the resistance to ozone that is too low, or whether the rate of stress decay is not sufficient, in order to proceed with further development. Measuring each property independently of the other is thus of real value to the compounder.

Exposure of various vulcanizates to the products of electrical discharge at pressures between 1.0 and 10 mm of mercury has shown that the atomic oxygen present under these conditions is a powerful cutting agent for butyl insulations which are quite resistant to ozone and to corona at atmospheric pressure. Natural rubber and SBR compounds which are vulnerable to ozone were found to resist cutting in atomic oxygen. Neoprene and Hypalon resist cutting by either ozone or atomic oxygen.

SUMMARY

The results of experiments on the ozone and corona cutting of rubber high voltage insulation show that the relaxation of mechanical stress in the insulation plays an important role. Studies were made to establish the stress decay characteristics of various formulations based on natural rubber, SBR and butly rubber. A method was developed for correlating the stress decay and ozone resistance characteristics which permits the performance of bent samples of any formulation to be predicted at ozone concentrations up to 0.2%. Comparisons were made between the cutting in an intense corona discharge and that in high concentrations of ozone outside of the discharge. These comparisons show that the results of ozone tests at constant load together with stress relaxation tests may be used to predict the performance of rubber insulation in corona discharge.

Tests were carried out in the products of corona discharge at pressures less than atomospheric. These tests lead to the conclusion that at very low pressures (ca. 1 mm Hg) cutting is caused not by ozone but by atomic oxygen. Compounds based on a variety of polymers were exposed to atomic oxygen and it was found that butyl rubber cuts rapidly in atomic oxygen while natural rubber, SBR, neoprene, and Hypalon do not. Antioxidants do not protect butyl rubber against cutting in atomic oxygen, but surface coatings were found to offer protection.

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[4] Dravnieks, *J. Am. Chem. Soc.* **72**, 3761 (1950).
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FACTORS INFLUENCING THE OZONE RESISTANCE OF NEOPRENE VULCANIZATES UNDER FLEXURE *

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The need for dynamic testing conditions, such as mild flexing, to study the attack of ozone on elastomeric vulcanizates, has become increasingly apparent. Many rubber goods, such as belts, tire sidewalls, and hose, are subjected to intermittent or continuously fluctuating strains in service and to evaluate their ozone resistance under constant stress or strain conditions is unrealistic and often leads to entirely erroneous conclusions. For example, it is well known that under static strain a vulcanizate's ozone resistance is enhanced by compounding with a wax which migrates to its surface and forms a protective film. However, numerous investigators[2,4,9,11,12] have reported that when a wax film is continuously ruptured by dynamic testing, the vulcanizate is even more vulnerable to ozone attack than if no wax were present. Other surface films also may act detrimentally under dynamic conditions. One such film may form under static exposure by the migration of antiozonants to the surface of a sample where they or their ozone reaction products provide a shield against ozone[1,3,8]. Also, diene elastomers, even when not under stress, react with ozone without cracking and it has been postulated that the thin films formed as a result of this reaction are less extensible[16] and consequently more subject to rupture on flexing than the unreacted rubber beneath them. It may well be found that the resistance of any surface barrier to dynamic stresses is the limiting factor for many products in service. Consequently, techniques for testing under dynamic conditions are needed at least to supplement testing under constant stress or strain in ozone.

Ozone exposure under dynamic conditions may prove to have analytical advantages over the static method. First, because dynamic tests accelerate ozone attack over that obtained statically[10,12,13] even though no increased strain is impressed. This permits the more ozone resistant elastomers to be tested at lower concentrations of ozone than would be possible statically. By testing in more dilute ozone, the correlation between results obtained under atmospheric exposure and the ozone cabinet should be better. Also, it seems likely that compounding ingredients which improve ozone resistance under dynamic conditions should provide improvement under static conditions as well, even though the converse is not necessarily true.

TEST APPARATUS

The ozone exposure chamber is a 4.5 cu ft rectangular box made of Lucite. Ozone concentrations within the chamber can be controlled within the range of 25 to 1000 parts per hundred million parts of air by varying the voltage on the ozone source, an Hanovia 93-A ultraviolet tube. Dry, compressed air is intro-

* An original contribution presented before the Division of Rubber Chemistry of the American Chemical Society, Los Angeles, California, May 14, 1959. Contribution No. 153.

duced into the cabinet at the rate of 0.5 cubic foot per minute. This is sufficient to take care of leakage and to enable a positive pressure to be maintained within the cabinet during those periods when air is being removed for ozone analysis. It has been reported[17] that rubber cracking is reduced considerably when air flow in the cabinet is not maintained at a reasonably high rate. In order to avoid the problem of stagnant, ozone depleted air around the exposed specimens, a fan with a capacity of 40 cubic feet per minute is situated behind the ultraviolet tube. With this fan, the ozone containing air is recirculated through the chamber approximately nine times per minute. During operation, the temperature of this air is maintained at 100° ± 2° F.

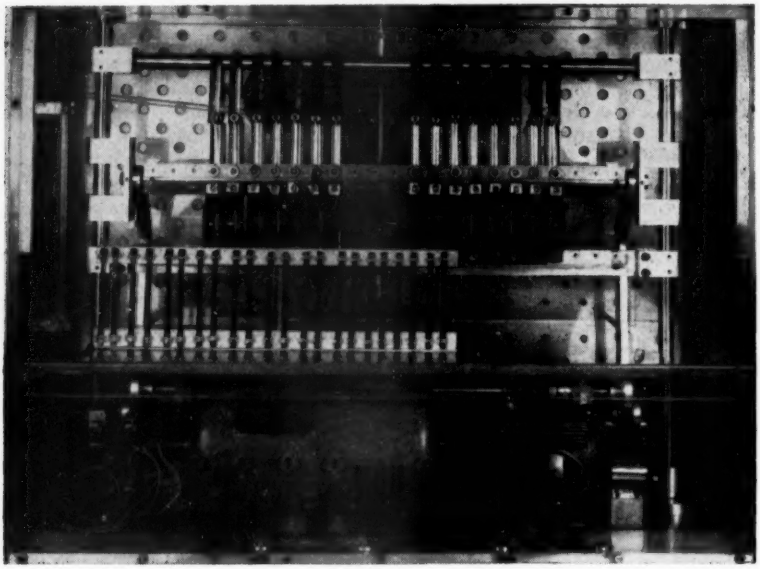

FIG. 1.

A flexing machine in the chamber is capable of inducing cyclic stresses by three methods. None of these methods are vigorous tests, such as are employed to study flex fatigue. The flexing is intended merely to continually disturb and produce strains on the surface of the test specimens to permit ozone attack but not to cause failure by excessive heat generation or mechanical breakdown. The first or "roller" method simply involves moving a test specimen back and forth over a roller. The second or "bent loop" method produces cyclic strains by first bending the sample double on itself and then straightening it out flat. The third or "tension" method gives the specimen a straight tension pull, followed by a complete relaxation of stress.

Three essential components of the flexing system can be seen in Figure 1. They include a $\frac{15}{16}$" diameter roll and two rectangular bars, approximately 24" long, $1\frac{1}{2}$" high and $\frac{3}{8}$" thick, supported on stationary posts. The upper bar is driven up and down the posts, a total distance of 2.5" by means of a cam device

connected to a rotating shaft and motor located beneath the ozone chamber. Flexing frequencies are adjustable up to 60 cycles per minute by a variable drive on the motor.

With the "roller" method, one end of a press cured fabric-backed (10 oz duck) rectangular specimen ($0.075'' \times \frac{9}{16}'' \times 6''$) is connected to the movable bar by a hook through a grommet reinforced $\frac{3}{16}''$ hole in the specimen. The other end of the specimen is placed over the roller (fabric side down) and attached, in the same manner, to an 18 oz weight. As the bar moves up and down at the desired frequency, a maximum strain of approximately 18% is induced in the specimen by the curvature of the roller. Machines producing the same flexing action are located at exposure stations in Delaware and Florida, so that a correlation between outdoor and ozone cabinet exposure eventually can be obtained using this "roller" method.

RATING SYSTEM

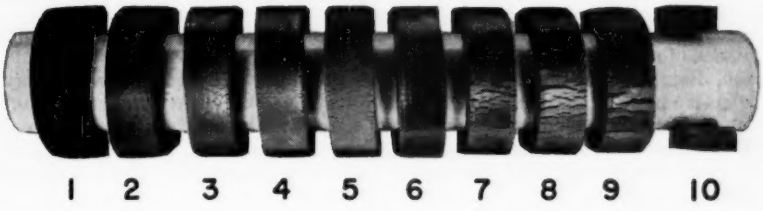

FIG. 2.

With the "bent loop" method, a $6'' \times \frac{1}{2}'' \times \frac{1}{4}''$ press cured specimen is connected between the lower stationary bar and the upper movable bar. By fixing the stationary bar at the proper distance from the movable bar, there is no strain on the straightened specimen with the movable bar at its highest point in the cycle. However, when this bar moves to its lowest point in the cycle and the specimen is bent double, a maximum strain of 25% is produced on the outside center surface of the vulcanizate.

The "tension" method can be used in conjunction with the "roller" method but not the "bent loop" method. It gives the test specimen ($\frac{1}{4}'' \times 6'' \times 0.075''$) a cyclic tension pull between the two bars on the machine. In this case, however, maximum strain exists with the movable bar in its uppermost position and no strain when it is in its lowest position.

The machine accommodates 24 specimens for each flexing method. All metal parts within the ozone cabinet are constructed of either aluminum or stainless steel. Adequate space is available within the ozone chamber for static exposure of $6'' \times \frac{1}{4}'' \times 0.075''$ specimens mounted on varnished wooden frames.

TEST PROCEDURES

Data will be shown for both the "bent loop" and "roller" test methods. The flexer was operated at a frequency of 10 cycles per minute and ozone concentration was maintained at either 60 or 300 parts per hundred million parts of air, depending on the severity of exposure desired. In addition, specimens

were tested statically in the same environment under 20% strain and, in some cases, under 40% strain as well.

Ozone determinations were made daily by withdrawing air from the middle of the chamber through a hole in the top of the box and by analyzing, using the Crabtree and Kemp Method as described in ASTM D-1149-55T. The ozone concentration in the chamber was maintained within $\pm$ 8% of the desired concentration over extended runs with this system.

Observations of the damage to specimens due to ozone attack were made 3 times daily. A rating system of 1 to 10 (Figure 2) was used to assess the degree of cracking. The time to a rating of 3 on the above scale was taken as an end point in reporting results. This criterion has the advantage over "time-to-first-evidence-of-damage" used by other investigators[5,7,13], as the end point could be determined by interpolation if a severity rating of 3 was exceeded between observations.

EFFECT OF COMPOUNDING INGREDIENTS IN NEOPRENE

TYPE OF ANTIOZONANT

Conventional rubber antioxidants have little effect in preventing ozone attack of natural rubber, SBR, and nitrile rubbers[6,11–14]. By contrast, Thompson, Baker, and Brownlow[15] have shown that certain antioxidants are very effective in inhibiting the ozone attack of noeprene vulcanizates under constant stress or strain conditions, provided they are present in sufficient concentration. Therefore, when antioxidants are used in relatively high concentrations in neoprene (3 or more parts) the designation antiozonant is appropriate and will be used herein.

The first study involved testing the effectiveness of 20 proprietary materials at the 5 part level as antiozonants for cured Neoprene Type W compounds exposed to 300 pphm ozone. A base compound (shown in Table I) was mixed on a 36-inch mill and then the various additives were incorporated into the base compound on a 16-inch mill. Some of the antiozonants studied were known to affect rate of cure, therefore, a very safe curing system (a combination of a thiuram, a guanidine and sulfur) was used so that the effect of antiozonant type on scorch rate would be readily apparent. Mooney scorch tests were made on all freshly mixed compounds and in order to obtain an indication of the bin storage stability of the compounds, this test was repeated after they had been stored for 2 weeks at 100° F. Three controls were included in this first study. One contained no antioxidant (or antiozonant), another contained 2 parts N-phenyl-1-naphthylamine (a normal quantity of antioxidant for a compound of this type) and the third control contained 5 parts wax but no antioxidant. The results of the ozone and scorch tests are summarized in Table I in order of increasing antiozonant effectiveness. The antiozonants are divided into 3 groups. Group 1 contains the controls and those additives that had no appreciable effect on ozone resistance. Group 2 contains those antiozonants that had a moderate effect in delaying ozone attack and Group 3 shows those that were highly effective.

The hindered phenols were of no benefit as evaluated by dynamic tests and constant strain tests showed they even had a slight adverse effect when compared to the control with no antioxidant or wax. The cured compound containing only 2 parts of antioxidant (N-phenyl-1-naphthylamine) was somewhat better in ozone resistance than the one with no antioxidant but this level

Table I

Effect of Antiozonant Type on Ozone Resistance and Scorch Rate of Neoprene Type W

(Ozone Concentration—300 pphm)

Base Compund

Neoprene Type W	100.00
Magnesia	4.00
Stearic acid	0.50
Hard clay	70.00
SRF carbon black	30.00
Process oil	15.00
Zinc oxide	5.00
Tetramethylthiuram monosulfide[1]	0.50
Di-ortho-tolylguanidine[2]	0.50
Sulfur	1.00

Cure—25 minutes at 153° C (307° F)

Type additive	Trade name	Amount	Dynamic testing: Bent loop (Time to rating of 3)	Dynamic testing: Roller (Time to rating of 3)	Static testing 20% strain (hrs. to break)	Mooney scorch (min. to 5 pt. rise): Orig.	Mooney scorch (min. to 5 pt. rise): After 2 wks. at 100° F
Group 1							
None	—	—	<12	12	59	>45	40
N-phenyl-1-naphthylamine	Neozone A[3]	2	<12	17	73	>45	38
Mixture of petroleum waxes	Heliozone[3]	5	<12	<12	66	>45	>45
Hindered phenol	Zalba[3]	5	<12	12	49	35	36
2,2′-methylene bis(4-methyl-6-*tert*-butylphenol)	Antioxidant 2246[4]	5	<12	12	49	35	36
4,4′-thio-bis(6-*tert*-butyl-*m* cresol)	Santowhite Crystals[5]	5	12	17	88	21	12

[1] Thionex, E. I. du Pont.
[2] DOTG, E. I. du Pont.
[3] E. I. du Pont.
[4] Calco.
[5] Monsanto.

TABLE I (*Continued*)

Type additive	Trade name	Amount	Dynamic testing: Bent loop (Time to rating of 3)	Dynamic testing: Roller (Time to rating of 3)	Static testing 20% strain (hrs. to break)	Mooney scorch (min. to 5 pt. rise): Orig.	Mooney scorch (min. to 5 pt. rise): After 2 wks. at 100° F
Group 2							
N,N′-di-2-naphthyl ppd*	Agerite White[6]	5	25	34	66	34	28
Mixture of octylated diphenylamines	Octamine[7]	5	30	44	97	>45	38
N-phenyl-1-naphthylamine	Neozone A[3]	5	30	34	97 (9)**	44	32
N,N′-diphenylethylene diamine	Stabilite[8]	5	34	41	97 (4)	8	Set up
N-phenyl-2-naphthylamine	Neozone D[3]	5	34	41	97 (OK)	36	20
Group 3							
Butyraldehyde-aniline condensation prod.	Antox[3]	5	41	59	97 (OK)	26	6
Nickel dibutyldithiocarbamate	NBC[3]	5	41	59	97 (OK)	45	40
Diphenylamine-acetone condensation prod.	BLE-25[7]	5	41	62	97 (OK)	25	11
N,N′-di-2-octyl-ppd	UOP288[9]	5	49	59	97 (OK)	8	Set up
.65 N-phenyl-1-naphthylamine .35 N,N′-diphenyl ppd	Akroflex C[3]	5	54	59	97 (OK)	22	10
N,N′-di-3-(5-methyl-heptyl)-ppd	UOP 88[9]	5	54	59	97 (OK)	16	Set up
1,2-Dihydro 2,2,4-trimethyl 6 ethoxy-quinoline	Santoflex AW[5]	5	54	88	97 (OK)	22	11
.65 N-phenyl-2-naphthylamine .35 N,N′-diphenyl ppd	Akroflex CD[3]	5	59	66	97 (OK)	21	8
.50 N-phenyl-2-naphthylamine .25 4,4′-dimethoxydiphenylamine .25 N,N′-diphenyl ppd	Thermoflex A[3]	5	63	93	97 (OK)	23	9
1,2-Dihydro-2,2,4-trimethylquinoline	Flectol H[5]	5	66	88	97 (OK)	4	Set up
1,2-Dihydro-2,2,4-trimethylquinoline	Agerite Resin D[6]	5	73	93	97 (OK)	7	Set up
Diphenylamine-acetone condensation prod.	Aminox[7]	5	80	97	97 (OK)	12	Set up

ppd*—p-phenylene diamine.
( )**—Rating at 97 hours.

[6] Vanderbilt.
[7] Naugatuck.
[8] C. P. Hall.
[9] Universal Oil Products.

of antioxidant was not adequate for good ozone protection either by dynamic or static tests. At this rather high concentration of ozone, and in the absence of antioxidant, 5 parts of wax had a slight adverse effect by dynamic tests and was only slightly beneficial in the static test. The effect of wax in combination with antiozonant will be treated more thoroughly later.

The chemicals of Group 2, while somewhat beneficial, were not outstanding from an antiozonant standpoint. However, with one exception (N,N′-diphenylethylene diamine), the Group 2 antiozonants did not affect scorch rate as greatly as the majority of those in Group 3 and so can be utilized with more assurance of processing safety. All the Group 3 antiozonants with the exception of nickel dibutyldithiocarbamate had an adverse effect on scorch rate but to a greatly varying degree. The mixture of 0.50 N-phenyl-2-naphthyl-

TABLE II

EFFECT OF ANTIOZONANT AND WAX CONCENTRATION ON NEOPRENE OZONE RESISTANCE

Base Compound
(Same as in Table I)

Cure—25 minutes at 153° C (307° F)

Antiozonant* concentration	Wax** concentration	60 pphm ozone			300 pphm ozone		
		Roller method	Bent loop method	Static 20% strain	Roller method	Bent loop method	Static 20% strain
		Hours to rating of 3			Hours to rating of 3		
—	—	41	20	32	9	7	7
—	4	62	20	41	7	7	12
1	—	65	41	49	15	9	12
3	—	186	89	355 (OK)	21	15	150 (OK)
5	—	220	162	355 (OK)	43	38	150 (OK)
7	—	331	307	355 (OK)	91	51	150 (OK)
9	—	>335	331	355 (OK)	99	58	150 (OK)
1	2	59	41	355 (OK)	15	9	15
3	2	162	130	355 (OK)	27	21	150 (OK)
5	2	250	186	355 (OK)	58	43	150 (OK)
7	2	>355	331	355 (OK)	91	67	150 (OK)
9	2	>355	>355	355 (OK)	99	91	150 (OK)
1	4	73	73	355 (OK)	15	10	150 (OK)
3	4	186	162	355 (OK)	27	30	150 (OK)
5	4	259	240	355 (OK)	34	34	150 (OK)
7	4	280	331	355 (OK)	51	58	150 (OK)
9	4	>355	>355	355 (OK)	99	82	150 (OK)

* Mixture of .50 N-phenyl-2-naphthylamine, .25 4,4′-dimethoxydiphenylamine, and .25 N,N′-diphenyl *p*-phenylene diamine, Thermoflex A, E. I. du Pont.
** Heliozone, E. I. du Pont.

amine, 0.25 4,4′-dimethoxydiphenylamine, and 0.25 N,N′-diphenyl-*p*-phenylenediamine provided a higher degree of ozone resistance than most of the chemicals in this group, yet it rated well in scorch resistance and bin storage stability.

In order to check for antiozonant bloom, cured slabs of each compound were sandwiched together and observed after 2 months storage in the dark at 75° F. A heavy white bloom was apparent on the surface of two vulcanizates; the one containing 4,4′-thio-bis-(6-*tert*-butyl-m-cresol) and the one containing a mixture of 0.65 N-phenyl-1-naphthylamine and 0.35 N,N′-diphenyl-*p*-phenylenediamine.

AMOUNT OF ANTIOZONANT AND WAX

The next experiment was designed to study the effect of antiozonant concentration (1 to 9 parts) without and in combination with 2 and 4 parts wax.

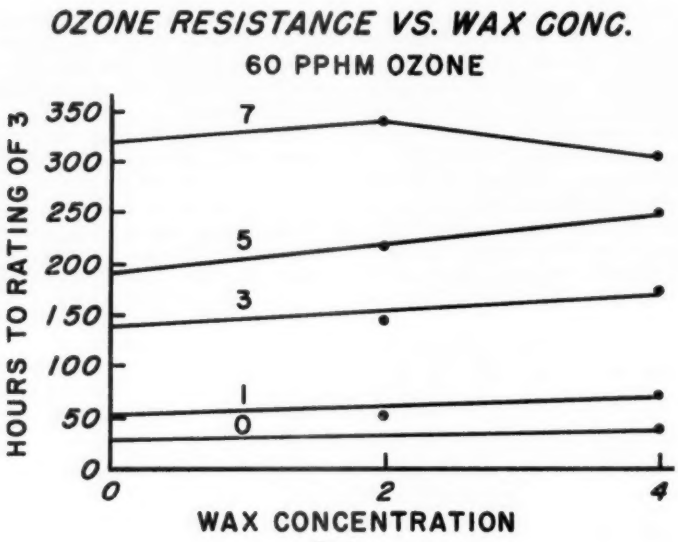
OZONE RESISTANCE VS. WAX CONC.
60 PPHM OZONE
HOURS TO RATING OF 3
350
300
250
200
150
100
50
0
7
5
3
1
0
0
2
4
WAX CONCENTRATION

Fig. 3.

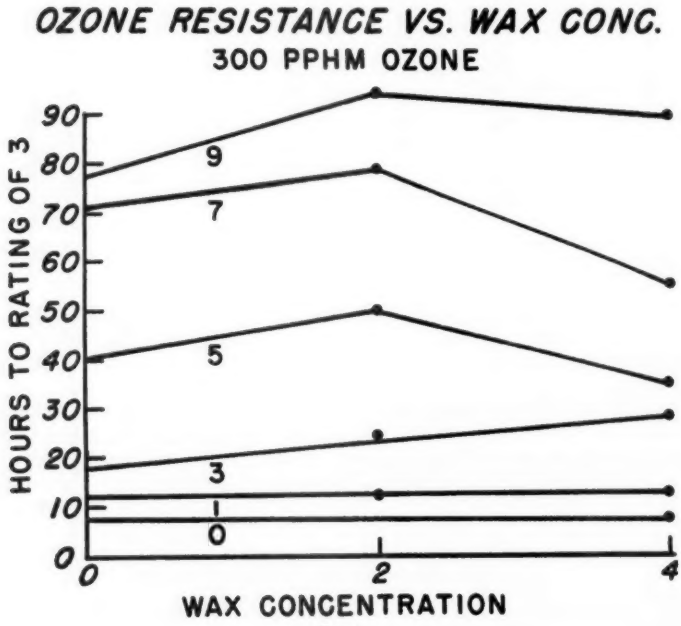
OZONE RESISTANCE VS. WAX CONC.
300 PPHM OZONE
HOURS TO RATING OF 3
90
80
70
60
50
40
30
20
10
0
9
7
5
3
1
0
0
2
4
WAX CONCENTRATION

Fig. 4.

The same base compound was used as in the first experiment. The antiozonant chosen for this study was a mixture of 0.50 N-phenyl-2-naphthylamine, 0.25 4,4′-dimethoxydiphenylamine and 0.25 N,N′-diphenyl-*p*-phenylenediamine, as it performed favorably in the first comparison at the 5 part level.

Table II summarizes the results obtained at both 60 and 300 pphm ozone using both dynamic test methods, as well as the static method at 20% strain. As was the case in the first experiment, the two dynamic test methods showed similar trends but the "bent loop" test was, in general, slightly more severe than the "roller" test, probably because of the higher maximum strain impressed (25% vs. 18%).

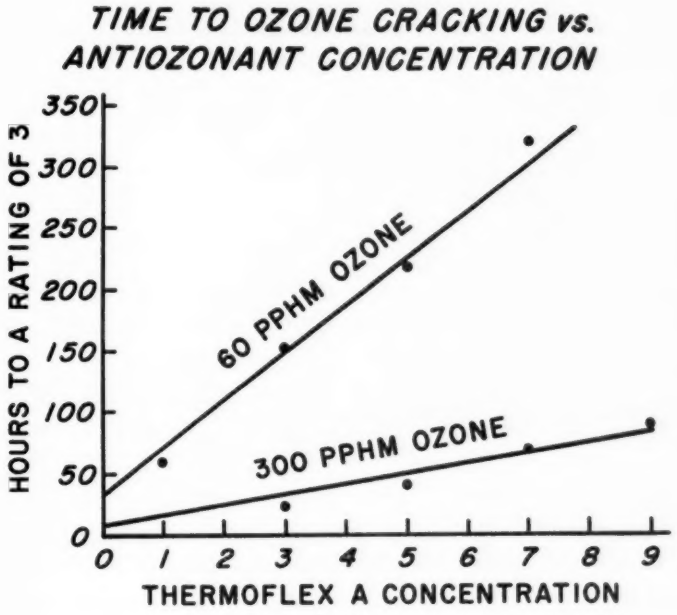

FIG. 5.

The effect of wax concentration in combination with increasing amounts of antiozonant at two different ozone concentrations is shown in Figures 3 and 4. These results were derived from the data shown in Table II by averaging the results obtained by the two dynamic test methods. Figure 3 is a plot of time to ozone attack (rating of 3) at 60 pphm ozone vs. wax concentration at the various levels of antiozonant, and Figure 4 is a similar plot for the results obtained at 300 pphm ozone. Contrary to results reported with other elastomers[2,4,9,11,12], 2 parts of wax did not impair dynamic ozone resistance, but rather was somewhat beneficial in noeprene. Even 4 parts of wax was beneficial in the 60 pphm ozone test, except with the highest level of antiozonant. However, increasing the wax from 2 to 4 parts impaired ozone resistance somewhat in the 300 pphm ozone test, when 5 or more parts of antiozonant were present.

The effect of increasing antiozonant from 0 to 9 parts is shown in Figure 5 where time to ozone attack at both ozone concentrations is plotted against antiozonant concentration. These data are derived from Figures 3 and 4 by averaging the results obtained with 0, 2 and 4 parts wax. This shows that ozone resistance under dynamic conditions increases quite linearly with increasing antiozonant concentration and that, in the range of ozone concentrations studied, time to ozone attack is very nearly proportional to ozone concentration since the slope of the line for 300 pphm is about $\frac{1}{5}$ the slope of the

TABLE III

EFFECT OF TYPE AND AMOUNT OF FILLER ON NEOPRENE OZONE RESISTANCE

(Ozone Concentration—330 pphm)

Base Formula

Neoprene Type W	100
Mixture of:	
0.50 N-phenyl-2-naphthylamine[1]	
0.25 4,4′-dimethoxydiphenylamine[1]	
0.25 N,N′-diphenyl-*p*-phenylene diamine[1]	3
Stearic acid	0.5
Magnesia	4.0
Zinc oxide	5.0
2 mercapto imidazoline[2]	0.5
Filler	As shown
Light process oil	As shown

Cure—25 minutes at 153° C (307° F)

Type filler	Volumes filler/ 100 volumes neoprene	Volumes oil/ 100 volumes neoprene	Stress at 200% psi	Dynamic tests Hours to rating of 3		Static test 20% strain
				Bent loop	Roller	
MT carbon black	None	None	175	210	>210	210 (OK)
	20	4	250	183	>210	210 (OK)
	40	8	575	150	200	210 (OK)
	80	16	1325	93	120	210 (OK)
Whiting[3]	20	4	200	159	210	210 (OK)
	40	8	250	130	159	210 (OK)
	80	16	250	90	102	210 (OK)
Hard clay	20	4	550	159	165	210 (OK)
	40	8	925	130	150	210 (OK)
	80	16	1600	31	49	210 (OK)

[1] Thermoflex A, E. I. du Pont.
[2] NA–22, E. I. du Pont.
[3] Atomite, Thompson, Weinman.

line for 60 pphm. The cured stocks containing greater than 5 parts of antiozonant displayed a bloom a few days after cure. This bloom was probably caused by the migration of N,N′-diphenyl-*p*-phenylenediamine, the least soluble ingredient in the antiozonant mixture. However, the presence of a bloom did not detract from or contribute to the ozone resistance of these vulcanizates as the slope of the lines in Figure 5 did not change at antiozonant concentrations above 5 parts.

A linear plot similar to Figure 5 could not be made from the results of static testing in ozone. This was because when no antiozonant or very low concen-

trations of antiozonant were present, rate of attack was quite rapid; but once a threshold level of antiozonant and wax (which depends on ozone concentration and degree of strain) was exceeded, no sign of attack was observed even up to the completion time of the test.

TABLE IV

EFFECT OF TYPE OF PLASTICIZER ON NEOPRENE OZONE RESISTANCE

(Ozone Concentration—60 pphm)

Base Compound	
Neoprene Type W	100.0
Mixture of:	
0.50 N-phenyl-2-naphthylamine[1]	
0.25 4,4′-dimethoxydiphenylamine[1]	
0.25 N,N′-diphenyl *p*-phenylene diamine[1]	3.0
Stearic acid	0.5
Magnesia	4.0
MT carbon black	117.0
Zinc oxide	5.0
2 mercapto imidazoline[2]	0.5
Plasticizer (as shown)	13.0

Cure—25 minutes at 153° C (307° F)

Type plasticizer	Trade name	Dynamic tests Hours to a rating of 3		Static test 20% strain
		Bent loop	Roller	
Coumerone-indene resin	Cumar MH 24[3]	95	102	210 (OK)*
Polyether	TP 90 B[4]	95	110	210 (OK)
Dioctyl sebacate	Monoplex DOS[5]	95	120	210 (OK)
Polymerized aromatic hydrocarbon	Kenflex A[6]	95	140	210 (OK)
Polymerized aromatic hydrocarbon	Resinex 100[7]	102	120	210 (OK)
Tricresyl phosphate	Celluflex 179A[8]	102	130	210 (OK)
Naphthenic petroleum oil	Circo Oil[9]	102	140	210 (OK)
Aromatic petroleum oil	Sundex 53[9]	102	140	210 (OK)
Aromatic petroleum oil	G. B. Light Process Oil[10]	102	150	210 (OK)
Butyl oleate	—	150	159	210 (OK)
Mixture of mono- and di-furfuryl acetone	Furatone 1547[11]	>210 (2)*	>210 (2)*	210 (OK)
Linseed oil—raw	—	>210 (OK)	>210 (OK)	210 (OK)

* Figure in parenthesis is rating at the completion of the test.
[1] Thermoflex A, du Pont.
[2] NA-22, du Pont.
[3] Barrett.
[4] Thiokol.
[5] Rohm and Haas.
[6] Kenrich.
[7] Harwick Standard.
[8] Celanese.
[9] Sun Oil.
[10] Golden Bear Oil.
[11] Irvington Varnish.

TYPE AND AMOUNT OF FILLER

The effect of type and amount of filler on the ozone resistance of neoprene was studied next. Vulcanizates containing 0, 20, 40 and 80 volumes of three different fillers (MT carbon black, hard clay and whiting) were compared. In this work the ratio of plasticizer to filler on a volume basis was kept constant at 1 to 5 and each compound contained 3 parts of a mixture of 0.50 N-phenyl-2-naphthylamine, 0.25 4,4′-di-methoxydiphenylamine and 0.25 N,N′-diphenyl-*p*-phenylenediamine.

The results of ozone tests run at 300 pphm are summarized in Table III. No ozone attack was noted on any of the samples exposed statically at 20% strain even after 210 hours, so once again the dynamic tests were required to assess the effect of the variables. They showed that with all three fillers,

TABLE V

EFFECT OF TYPE OF PLASTICIZER ON NEOPRENE OZONE RESISTANCE
(Ozone Concentration—300 pphm)

Base Compound
(Same as in Table IV)
Cure—25 minutes at 153° C (307° F)

		Hours to a rating of 3			
		Dynamic tests		Static tests	
Type plasticizer	Trade name	Bent loop method	Roller method	20% strain	40% strain
Naphthenic petroleum oil	Circo Oil[1]	15	21	>266 (OK)*	21
Mixture of mono- and di-furfuryl acetone	Furatone 1547[2]	58	67	>266 (OK)*	>266 (OK)*
Linseed oil—raw		212	>266 (2)*	>266 (OK)*	>266 (OK)*

* Rating at completion of test indicated in parenthesis.
[1] Sun Oil.
[2] Irvington Varnish.

ozone resistance decreased with increased loading and that greater loadings could be tolerated with MT carbon black than with the mineral fillers for a given degree of ozone resistance.

Modulus values also are shown in Table III. The rate of ozone attack does not correlate well with modulus for vulcanizates having the same amount (but different type) of loading. This indicates that neoprene's ozone resistance is not closely related to degree of stress on the specimen and confirms previous findings with neoprene tested statically[15] and natural rubber tested under dynamic ozone exposure[12].

TYPE OF PLASTICIZER

Neoprene ozone resistance depends considerably on the type of plasticizer used. Twelve different plasticizers were compared in the same base formulation. The results of ozone testing at 60 pphm are given in Table IV with the test data arranged in order of increased vulcanizate ozone resistance.

All the compounds containing petroleum oils had comparable ozone resistance even though the oils varied considerably in composition. The vulcanizates containing petroleum oils were somewhat more ozone resistant than those containing resinous hydrocarbons, a polyether and all but one of the ester plasticizers. This exception was butyl oleate which proved to be somewhat more beneficial than petroleum oil, probably due to its slight degree of unsaturation. The vulcanizate containing a furan derivative was so much better than the ones containing petroleum oil that this material can be classified as an antiozonant for neoprene. However, even more outstanding was the one containing linseed oil which was flexed for 210 hours without cracking. The vulcanizates containing linseed oil and the furan derivative were re-evaluated at 300 pphm ozone and compared to a control containing one of the petroleum plasticizers. At this higher concentration of ozone (Table V) the three ranked once again in the same order as at the lower ozone concentration and linseed oil provided outstanding ozone resistance for periods of over 200 hours.

LINSEED OIL

The exceptionally good results obtained with linseed oil under dynamic testing conditions confirms previously reported results[13] showing it to be an

excellent additive for neoprene when tested under static ozone exposure in tension. Although unsaturated oils, such as linseed, will protect neoprene, the writer and others[4,14] have found them to be of little or no effect in protecting SBR or natural rubber.

Certain materials which are antiozonants for freshly cured compounds are limited in practical value because they are either pro-oxidants or are fugitive due to their high degree of volatility[3]. The next experiment was designed to determine whether linseed oil would be undesirable from either standpoint. The series of compounds in Table VI show increasing amounts of linseed oil

TABLE VI

EFFECT OF LINSEED OIL ON HEAT AND OXYGEN BOMB AGING OF NEOPRENE

Neoprene Type W	100	100	100	100
N-phenyl-1-naphthylamine[1]	3	3	3	3
Stearic acid	0.5	0.5	0.5	0.5
Magnesia	4.0	4.0	4.0	4.0
MT carbon black	125.0	125.0	125.0	125.0
Process oil	15.0	10.0	5.0	—
Linseed oil—raw	—	5.0	10.0	15.0
Zinc oxide	5.0	5.0	5.0	5.0
2 mercapto imidazoline[2]	0.5	0.5	0.5	0.5
Mooney Scorch at 121° C (250° F)—small rotor				
Minimum viscosity	19	21	19	20
Minutes to a 10 point rise	12.5	12.5	12	12
Cure—15 minutes at 153° C (307° F)				
Original				
Stress at 100%, psi	500	500	500	450
Tensile strength, psi	1700	1675	1725	1725
Elongation, %	380	380	380	380
Durometer hardness	67	67	65	67
After 7 days heat aging at 121° C (250° F) ASTM D 865-54T				
Stress at 100%, psi	1125	1050	1100	1250
Tensile strength, psi	1800	1775	1775	1800
Elongation, %	180	200	180	180
Durometer hardness	79	79	79	80
After 2 weeks oxygen bomb aging—ASTM D 572-53				
Stress at 100%, psi	650	650	625	600
Tensile strength, psi	1625	1525	1575	1550
Elongation, %	300	280	300	300
Durometer hardness	71	70	70	71
Cure—25 minutes at 153° C (307° F)				
Dynamic ozone resistance—60 pphm ozone Hours to a rating of 3 by "Roller" method				
Original	35	58	237	>333 (OK)
After 1 week at 100° C (212° F)	54	97	245	>333 (OK)

[1] Neozone A, du Pont.
[2] NA-22, du Pont.

Table VII

Formulas and Stress–Strain Properties of Vulcanizates Used to Compare Ozone Resistance of Different Elastomers

	7-A	7-B	7-C	7-D	7-E	7-F	7-G	7-H	7-I	7-J	7-K	7-L	7-M
Neoprene Type W	100	100	50	—	—	—	—	50	—	—	—	—	—
SBR 1500	—	—	50	100	100	100	—	—	—	—	—	—	—
Hypalon 20[1]	—	—	—	—	—	—	100	50	—	—	—	—	—
Smoked sheets	—	—	—	—	—	—	—	—	100	—	—	—	—
Butyl 365	—	—	—	—	—	—	—	—	—	100	—	—	—
NBR (medium nitrile)	—	—	—	—	—	—	—	—	—	—	100	—	—
Paracril Ozo[2]	—	—	—	—	—	—	—	—	—	—	—	100	—
Viton A[1]	—	—	—	—	—	—	—	—	—	—	—	—	100
Magnesia	4	4	2	—	—	—	—	—	—	—	—	—	15
N-phenyl-1-naphthylamine[3]	2	2	2	2	2	2	—	2	2.0	—	2.0	2.0	—
Mixture[4] of:													
(0.50 N-phenyl-2-naphthylamine) (0.25 4,4′-dimethoxydiphenylamine) (0.25 N,N′-diphenyl *p*-phenylene diamine)	—	3	3	—	3	—	—	3	—	—	—	—	—
N,N-Di-3-(5-methyl-heptyl) *p*-phenylene diamine[5]	—	—	—	—	—	3	—	—	—	—	—	—	—
SRF carbon black	44	44	53	58	58	58	49	47	59	58	55	49	29
Red lead	—	—	—	—	—	—	—	20	—	—	—	—	—
Litharge	—	—	—	—	—	—	25	—	—	—	—	—	—
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	—	—	5.0	5.0	5.0	—	—
Stearic acid	0.5	0.5	0.5	2.0	2.0	2.0	—	—	2.0	2.0	1.5	1.0	—
Di-ortho tolylguanidine[6]	—	—	1.0	—	—	—	—	—	—	—	—	0.25	—
Tetramethyl thiuram monosulfide[7]	—	—	1.0	0.5	0.5	0.5	—	—	—	—	—	0.25	—
Tetramethyl thiuram disulfide[8]	—	—	—	—	—	—	—	—	—	1.0	—	—	—
2-Benzothiazolyl disulfide[9]	—	—	—	0.5	0.5	0.5	0.5	—	1.0	—	1.5	1.0	—
Dipentamethylenethiuram tetrasulfide[10]	—	—	—	—	—	—	2.0	1.0	—	—	—	—	—
Dioctyl phthalate	—	—	—	—	—	—	—	—	—	—	—	25	—
Hexamethylenediamine carbamate[11]	—	—	—	—	—	—	—	—	—	—	—	—	1.0
2-Mercaptoimidazoline[12]	0.5	0.5	—	—	—	—	—	—	—	—	—	—	—
2-Mercaptobenzothiazol[13]	—	—	—	—	—	—	—	—	—	0.5	—	—	—
Sulfur	—	—	2.0	2.0	2.0	2.0	—	1.0	2.75	2.0	1.5	1.5	—
Cure time at 153° C (307° F) minutes	20	20	20	20	20	20	20	20	20	30	30	30	30 Plus 24 hr at 400° F
Stress at 100%, psi	550	450	600	500	475	400	1700	1000	450	325	426	350	750
Tensile strength, psi	3250	3000	2800	2400	2200	1900	2425	2400	3200	1225	2625	2800	2025
Elongation, %	360	400	280	320	340	320	140	260	500	360	380	700	240
Durometer hardness	68	68	68	66	67	63	72	73	73	65	67	58	75

[1] E. I. du Pont.
[2] Naugatuck Chemical.
[3] Neozone A, E. I. du Pont.
[4] Thermoflex A, E. I. du Pont.
[5] UOP 88, Universal Oil Products.
[6] DOTG, E. I. du Pont.
[7] Thionex, E. I. du Pont.
[8] Thiuram M, E. I. du Pont.
[9] MBTS, E. I. du Pont.
[10] Tetrone A, E. I. du Pont.
[11] DIAK No. 1, E. I. du Pont.
[12] NA-22, E. I. du Pont.
[13] MBT, E. I. du Pont.

(0 to 15 parts) with the petroleum oil concentration decreasing a corresponding amount in order to maintain a total of 15 parts plasticizer in each compound. The results of Mooney scorch, stress-strain (original and after oxygen bomb and heat aging) and dynamic ozone testing (original and after heat aging) are given in this table. Increasing amounts of linseed oil had no effect on scorch rate or stress-strain properties (either original or after heat or oxygen bomb aging). In all cases, the vulcanizates improved somewhat in ozone resistance after heat aging for one week at 100° C (212° F). The vulcanizate containing 5 parts of linseed oil displayed only a modest improvement in ozone resistance over the one containing no linseed oil. This would indicate that linseed oil is not as efficient an antiozonant on an equivalent weight basis as many of the antiozonants shown in Group 3 of Table I. However, 10 parts of linseed oil gave a considerable improvement in resistance to ozone attack and the vulcanizate containing 15 parts of this unsaturated vegetable oil did not crack even after 300 hours dynamic exposure at 60 pphm ozone. Due to its high compatibility in neoprene and neutral effect on scorch, these relatively high amounts are not prohibitive.

TABLE VIII

LESS OZONE RESISTANT VULCANIZATES

(Ozone Concentration—60 pphm)

Compound number (formulas shown in Table VII)	Elastomer	Hours to a rating of 3		
		Dynamic tests		
		Bent loop	Roller	Static test 20% strain
7-K	Nitrile	12	15	15
7-D	SBR 1500	16	20	20
7-I	Natural rubber	16	28	16
7-L	Paracril Ozo	24	24	>160 (OK)
7-E	SBR 1500*	36	42	24
7-F	SBR 1500**	43	84	>160 (OK)

* Compound contained 3 parts of mixture of 0.50 N-phenyl-2-naphthylamine, 0.25 4,4'-dimethoxydiphenylamine and 0.25 N,N'-diphenyl p-phenylene diamine, Thermoflex A, du Pont.
** Compound contained 3 parts N,N'-di-3-(5 methyl-heptyl) p-phenylene diamine, UOP 88, Universal Oil Products.

COMPARISON OF ELASTOMERS AND ELASTOMER BLENDS

The data so far presented were for neoprene compositions only. The next experiment was designed to compare the dynamic ozone resistance of 13 vulcanizates prepared from 8 different commercial elastomers as well as 50–50 blends of several of them. Each compound contained 30 volumes of SRF carbon black per 100 volumes of elastomer. The formulas and results of vulcanizate stress-strain tests are shown in Table VII.

Initially, all of the vulcanizates were exposed to an ozone concentration of 60 pphm. The 6 vulcanizates that showed an ozone attack rating of 3 in 85 hours or less under dynamic conditions are grouped in Table VIII. The remaining 7 vulcanizates which survived the 60 pphm exposure were retested at an ozone concentration of 300 pphm. Table IX gives the results of testing these more resistant vulcanizates in the higher concentration of ozone.

Some interesting observations can be made by examining the data in Table VIII for the less ozone resistant vulcanizates. As would be expected, vulcanizates of nitrile (7-K), SBR (7-D), and natural rubber (7-I) showed relatively little ozone resistance when compared to the others in this study. Three

parts of an antiozonant, N,N'-di-3-(5-methyl-heptyl) p-phenylenediamine, greatly improved the static ozone resistance of SBR and had a moderate effect in improving ozone resistance under dynamic conditions as well (7-F vs. 7-D). Although the addition of 3 parts of a flex crack inhibiting antioxidant to SBR rubber (7-E) produced no significant improvement in static ozone resistance, it was a beneficial additive by dynamic tests. The Paracril Ozo vulcanizate (7-L) was found to be very good in resistance to ozone attack under constant strain conditions but not outstanding by dynamic tests. The type of failure observed with Paracril Ozo under dynamic exposure was quite unique in that relatively few, but very deep cracks, were formed.

The excellent response of neoprene to antiozonant is shown once again in Table IX (7-B vs. 7-A), which gives the results of testing the more ozone resistant vulcanizates in a 300 pphm concentration of ozone. The butyl vulcanizate (6-K) was unusual because its resistance to ozone by dynamic tests was somewhat greater than by static tests. Also, the type of cracking noted with butyl was like that observed with the Paracril Ozo cured compound.

TABLE IX

HIGHLY OZONE RESISTANT VULCANIZATES

(Ozone Concentration—300 pphm)

Compound number (formulas shown in Table VII)	Elastomer	Hours to a rating of 3			
		Dynamic tests		Static tests	
		Bent loop	Roller	20% strain	40% strain
7-C	Neoprene-SBR* (50–50)	12	16	>266 (OK)	16
7-A	Neoprene	16	21	16	12
7-B	Neoprene*	75	92	>266 (OK)	>266 (OK)
7-J	Butyl	125	135	119	55
7-H	Neoprene-Hypalon* (50-50)	192	>266 (OK)	>266 (OK)	>266 (OK)
7-G	Hypalon	>266 (OK)	>266 (OK)	>266 (OK)	>266 (OK)
7-M	Viton	>266 (OK)	>266 (OK)	>266 (OK)	>266 (OK)

* Compound contained 3 parts of a mixture of 0.50 N-phenyl-2-naphthylamine, 0.25 4,4'-dimethoxydiphenylamine and 0.25 N,N'-diphenyl p-phenylene diamine, Thermoflex A, E. I. du Pont.

As might be expected, the 50–50 blend of neoprene and Hypalon (7-H) was more resistant to ozone attack than straight neoprene and the Hypalon (7-G) and the Viton (7-M) vulcanizates were completely unaffected by 300 pphm ozone even under dynamic testing conditions.

ACKNOWLEDGMENT

The author wishes to express his thanks to N. N. Mueller of the Du Pont Elastomers Laboratory Engineering Group who designed the ozone chamber and dynamic tester used for this work.

SYNOPSIS

The effect of compounding ingredients on the ozone resistance of neoprene vulcanizates is emphasized. Accelerated testing of these highly ozone resistane vulcanizates is accomplished by continuously flexing test specimens in an ozone chamber. Although many of the more effective antiozonants have a severt adverse effect on compound scorch rate, NBC (nickel dibutyldithiocarbamate) gives good ozone protection without affecting scorch. Thermoflex A (a mixture of aromatic secondary amines) provides even greater protection than NBC

yet impairs scorch only to a moderate degree. Neoprene's ozone resistance increases linearly with increasing antiozonant concentration but decreases with increasing amounts of filler. In the range of ozone concentrations studied (60 pphm to 300 pphm), ozone attack is proportional to ozone concentration. Linseed oil, unlike most other plasticizers, functions as a strong antiozonant in neoprene when 10 or more parts are present. In a comparison of the ozone resistance of vulcanizates prepared from a number of different elastomers and elastomer blends, it is shown that Hypalon* and Viton* (registered trademark for Du Pont's synthetic rubbers) are completely resistant to attack even under dynamic test conditions.

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OZONE CRACKING IN THE LOS ANGELES AREA *

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INTRODUCTION

During the early studies of Los Angeles air pollution, with its typical oxidant effect, it was observed that rubber goods marketed in this area were more severely cracked than those in any other part of the United States. This cracking was attributed to ozone, formed from the photochemical oxidation of organic material in the presence of nitrogen oxides[4,5,8]. Chemical methods using the liberation of iodine from potassium iodide solution, and spectroscopic methods, are now being used for spot analyses as well as continuous monitoring[12,13]. In addition, an inexpensive ozone test was developed, based on the time required to obtain initial cracking on a standard rubber test strip[1].

In a program conducted by the Armed Forces on the deterioration of rubber articles subject to long term exposure to atmospheric influences, the need was felt for a test which would allow an estimate of the cumulative effect of highly variable ozone concentration. The procedure adopted was a modification of the method described by Rugg[14], and consisted in exposing standard rubber test strips to outside air for a period of one week and measuring the sum of the depth of all the cracks. The total crack depth was then expressed in millimeters per hour.

This test, running parallel to the exposure of commercial rubber articles, has been carried out for more than three years on a weekly basis. During this period a wide variation in the degree of cracking was obtained, in some cases as great as 400 per cent. For a correct interpretation of outdoor testing of rubber articles it is of importance to know about these variations. The cumulative rubber test offers a convenient solution to this problem.

An important practical application is the testing of areas selected for outside storage of rubber goods. High ozone values have been found to occur in areas of poor ventilation—in enclosed yards where automobile exhausts furnish oxides of nitrogen and hydrocarbon needed to form ozone upon sunlight irradiation. This effect is enhanced by the chain reaction type of ozone formation. Laboratory experiments have shown that in the presence of ozone acceptors such as rubber ten times more ozone is formed than is indicated from the stoichiometric relation of the reactants[6,10]. We could expect then that in an enclosed area the production of ozone from nitrogen oxides and hydrocarbon will continuously produce cracking far in excess of the concentration of the pollutants.

DESCRIPTION OF TEST

The rubber stock is compounded according to the following recipe, a slight modification of that given by Bradley and Haagen-Smit[1]. The antiozonant

* An original contribution. Presented at the Los Angeles meeting of the Division of Rubber Chemistry, ACS, May 14, 1959. The present address of M. F. Brunelle is Los Angeles County Air Pollution Control District, Los Angeles, California. The present address of J. W. Haagen-Smit is Beckman Instruments Inc., 2500 Fullerton Road, Fullerton, California.

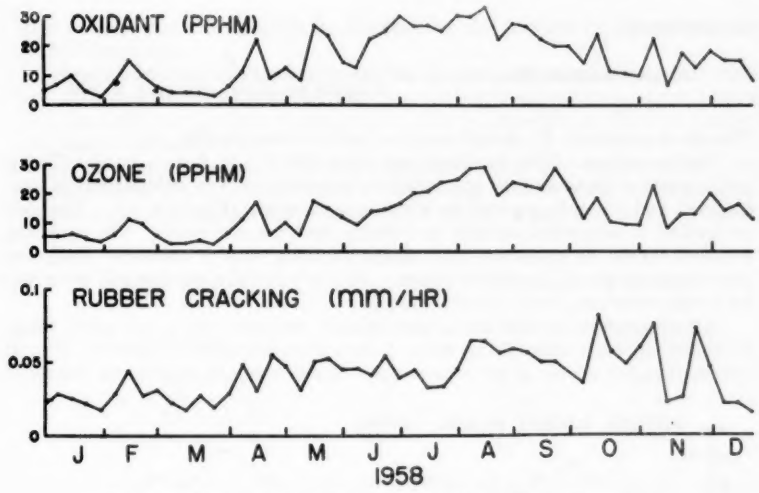

FIG. 1.—Rubber cracking vs. ozone and total oxidant, 1958, weekly average.

usually included in tire stocks is omitted to increase the sensitivity of the rubber test strip.

	Parts by weight
Rubber (Plantation)	100.00
Tire reclaim (Xylos No. 5484 or No. 6008)	125.00
SRF black	33.00
Stearic acid	1.50
Pine tar	8.00
Zinc oxide (F. C.)	4.00
Mercaptobenzothiazole	0.70
Sulfur	5.00

The cure is 40 minutes at 45 psi steam pressure.

At present, the rubber stock is obtained from Goodyear Tire and Rubber Co., Inc., 6701 South Central Ave., Los Angeles, where it is molded in 9 inch × 9 inch plaques at the development laboratory. Each batch should be calibrated against ozone before use, since slight differences in sensitivity may occur from batch to batch.

Calibration of rubber stock.—A laboratory ozonizer consisting of a Westinghouse Sterilamp (WL-794, 10-12 volts) set to deliver 0.2–0.5 ppm of ozone is calibrated against a 2 per cent potassium iodide solution. The standard rubber test strip (40 × 8 × 2 mm) (note: This size is standard for the *quantitative* test) is then folded on itself and placed in a tube of 13 mm diameter. The calibrated ozone stream is then drawn over the rubber at a rate of one liter per minute, and the time required to obtain initial cracking is noted. The stock is then assigned a constant number, K, equal to the product of the ozone concentration (ppm) and the time required to initial cracking (minutes) times 100: K = ozone concentration (ppm) × time to initial cracking (min) × 100

or, conversely,

$$\text{Ozone concentration (ppm)} = \frac{K}{\text{minutes to initial cracking} \times 100}$$

The stock constant, K, should vary no further than 85–100.

Test procedure.—The standard test strip (20 × 8 × 2 mm) (note: This is ½ *the length* of the standard quantitative test strip used in calibration) is bent on itself and the ends secured by winding with string (Figure 3, A). The loop so formed is suspended outside in a shady spot for one week. The sampling location should be protected from direct sunlight, rain or excessive wind, but the outside air should have free access. We have found a window sill, protected by a roof overhang, to be quite suitable.

After exposure for one week, the string is removed and a cut made longitudinally on each side of the strip, 1 mm from the edge (Figure 3, B). If necessary, after release of the tension the test pieces can be stored and measured

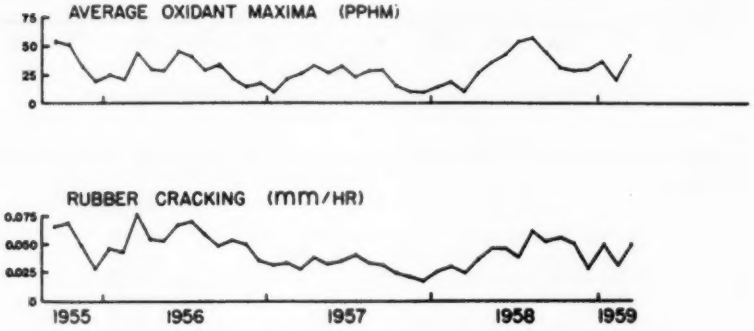

FIG. 2.—Cumulative rubber cracking vs. oxidant maxima, monthly average, Pasadena, California, 1955–1959.

at a convenient time. The total depth of the cracks obtained is measured under a microscope (100 ×) using an ocular micrometer, measuring both sides of the test strip, and taking the average of the total depth measured on each side (Figure 3, C). A holding device which enables us to apply slight tension to each strip facilitates the measurement by separating the cracks. The cracking is expressed as crack depth (mm/hr) and is obtained by dividing the average total cracking by the number of hours exposure.

CUMULATIVE RUBBER TEST IN AIR POLLUTION ANALYSIS

The cumulative test furnishes an index of the action of atmospheric ozone to which rubber articles are subjected in a certain area. The influence of varying weather conditions such as temperature and wind velocity on the degree of cracking on the test strips, as well as on the rubber articles, is an advantage and provides a more realistic estimate on the behavior of rubber exposed to the same variables.

The simplicity of the test would indicate its application to the determination of ozone distribution in air pollution studies. Its use would be comparable to

that of lead peroxide candles in determining the pattern of air pollution by sulfur compounds.

Before applying the method to testing of ozone concentration it was necessary to know the response of the standard rubber to different exposure times as well as to the temperature range which could be expected at different times of the year in different areas.

Effect of exposure time on cumulative rubber cracking.—Rubber strips were exposed for 2, 4, 6 and 8 days, and a comparison of the rubber cracking found at the end of these intervals is presented in Table I and Figure 4. A nearly

TABLE I

EFFECT OF EXPOSURE TIME ON CUMULATIVE RUBBER CRACKING

Exposure time	Total exposure, hrs	Total crack depth, mm	Average crack depth, mm/hr
4/21/58–4/23/58	48	4.36	0.091
4/21/58–4/25/58	96	9.90	0.103
4/21/58–4/27/58	148	15.1	0.102
4/21/58–4/29/58	192	17.3	0.090

linear relation between cracking and exposure time is evident. The average total cracking, expressed as mm/hr, did not fluctuate appreciably over the test period. On the same graph is shown the average total oxidant (determined with potassium iodide solution) over the same exposure periods. Here, too, a linear function is observed, which indicates a uniform period of air pollution during the experiment.

Temperature effects.—Standard test strips were exposed at different temperatures in the climate controlled "Earhart" greenhouse[15] for a period of one week. The results are shown in Table II.

TABLE II

EFFECT OF TEMPERATURE ON RUBBER CRACKING
(Strips Exposed for One Week in Earhart Greenhouse)

Temperature (° C)		Cracking	
Range	Average	Mm/hr	Average
26–20	23	0.0143	
		0.0223	0.0183
23–17	20	0.0175	
		0.0234	0.0204
20–14	17	0.0064	
		0.0060	0.0062
17–11	14	Not measurable	
13–7	10	Not measurable	
10–4	7	Not measurable	
Outside air			0.0348

The air entering the greenhouse is controlled by passage through filters before its temperature regulation, and the ozone concentration within the greenhouse is therefore considerably lower than outside. Nevertheless, a decided difference in the behavior of the rubber can be readily observed. At 17° C the cracking is much less than at 20° and 23° C, and below that temperature no measurable cracking could be found. It appears that 17° C is a critical temperature, below which our rubber stock loses its sensitivity to ozone cracking.

These results were confirmed by an experiment in which ozone at approxi-

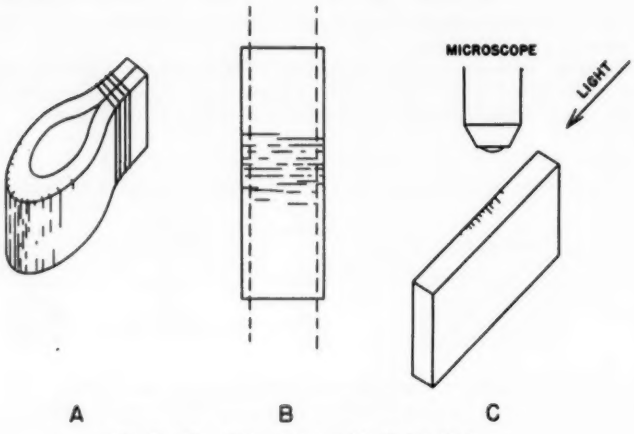

FIG. 3.—Cumulative rubber cracking test method.

mately 7 ppm was passed over bent rubber strips held at temperatures of 5, 12, 15, 18, 20, 24, 33 and 40° C. The flow rate was one liter per minute, and the exposure time 10 minutes. The results are shown in Figure 5. In this experiment the crack depth increases with temperature as a linear function above 18° C. Below that temperature the linear relationship no longer applies, and the sensitivity of the stock is greatly decreased. This may be caused by a change in the physical properties of the rubber stock at low temperatures, and for the extension of the application without the aid of complicating temperature controls, the use of rubber compounds with more favorable characteristics is being investigated.

Daily variation in rubber cracking.—While the cumulative rubber cracking over the two day exposure periods shown in Table I is apparently quite constant, a totally different picture is obtained when strips are exposed at different times of the day. In harmony with our previous findings on the photochemical origin of the ozone, we found that during the night the effect is small, and peak values are obtained during the day. Measurable cracking was obtained by

TABLE III

HOURLY VARIATION IN RUBBER CRACKING INTENSITY

Exposure time	Total exposure, hrs	Total crack depth, mm	Average crack depth, mm/hr
4/21/58–4/26/58 8 A.M.–12 Noon	20	4.38	0.219
4/21/58–4/26/58 12 Noon–5 P.M.	25	5.12	0.205
4/21/58–4/26/58 7 P.M.–6 A.M.	55	0.88	0.016
Total	100	10.38	
Average crack depth (100 hr)			0.103

exposing three groups of rubber strips at different intervals during the day for a period of six days. Table III shows the exposure times, and the results are presented in Figure 6. Also shown on the graph are the hourly average oxidant values determined over the test period by the liberation of iodine from potassium iodide solution. The positive correlation between the two phenomena is evident. Although the crack depth varies greatly during the day, the average total crack depth, expressed as mm/hr and computed for the 24 hour period, checks quite well with the averages obtained in the previous experiment of continuous night and day exposure. These results again indicate the additive nature of the ozone cracking within the limits of exposure used.

It has been observed that heavy cracking occurs especially during smog periods. The well established correlation between high ozone concentration and smog conditions is evident in the results of the cumulative test. Figures 1 and 2 illustrate the relation between these factors for samples taken in Pasadena by comparing the "oxidant", an expression of Los Angeles type smog, with the

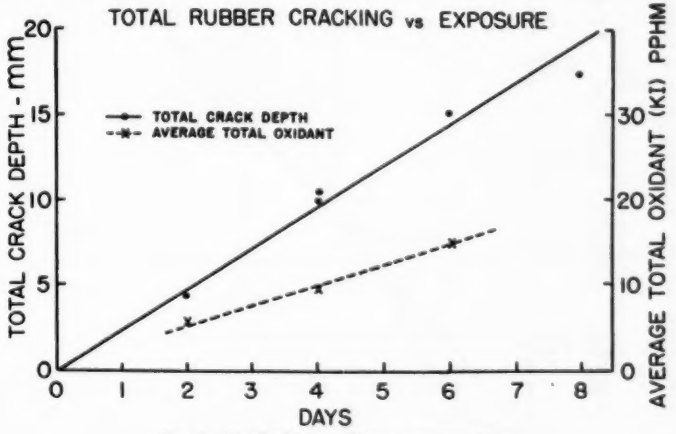

FIG. 4.—Total rubber cracking vs. exposure time.

rubber test. Figure 2 compares the monthly average obtained over a period of more than three years (September, 1955–March, 1959),with the oxidant maxima measured by the phenolphthalein method[9]. Figure 1 shows the weekly cumulative values, the weekly average of oxidant maxima, and the weekly average of ozone maxima during the year 1958. The ozone was measured by the quantitative rubber cracking method or by photometric measurement. Both oxidant and ozone were determined only during the daylight hours,whereas the cumulative rubber strips were continuously exposed for one week periods.

While generally good agreement has been found between the results of the cumulative rubber test and ozone and oxidant concentrations measured by chemical or physical analytical methods, there have been exceptional days on which relatively low cracking was observed when the oxidant or ozone concentration was high, or conversely, intensive rubber cracking was observed when these concentrations were low.

There are several reasons for this. The comparison is made with oxidant maxima obtained by chemical analysis during the daytime, while the cumulative

cracking integrates the activity over 7 days of 24 hour exposure. Some smog days show a high ozone value for only a short period, while other days are characterized by many hours of lower ozone concentration. For a more precise correlation, the 24 hour effects should be integrated. Also, the oxidant increase typical of Los Angeles type smog is attributed to the action of several oxidants besides ozone, among which the most significant are nitrogen oxides and organic peroxides. Only the ozone is responsible for the rubber cracking, however.

Another factor which affects the rate of rubber cracking is the change in stress which occurs in the rubber strip once cracking has begun. As the cracks deepen, the tension becomes less, and the rate of cracking tends to decrease.

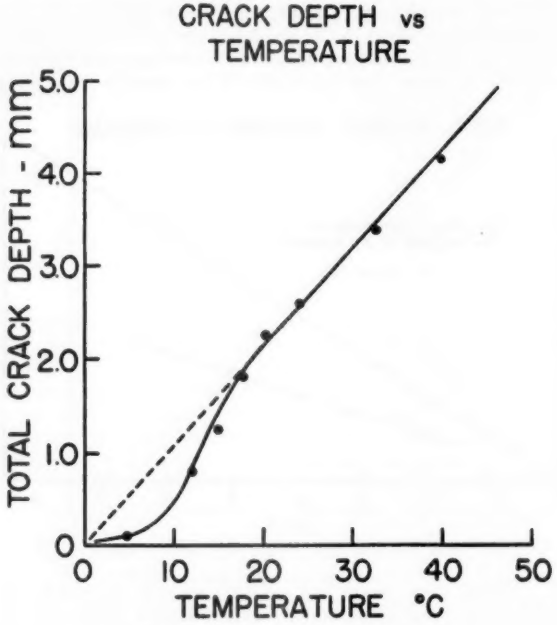

FIG. 5.—Crack depth vs. temperature.

For this reason, if high concentrations of ozone are anticipated, the exposure time should be adjusted so that the cracking does not become excessive. We have actually seen some of our test strips break in two when exposed for too long a time under severe conditions of air pollution.

Measurement of the cumulative rubber cracking in Wethersfield, Conn., has shown significantly lower values throughout the year than were obtained in Pasadena[7]. The low values obtained in Wethersfield during the colder months can be attributed to temperature effects. However, even during the summer months the cracking was 40 per cent more severe in Pasadena, verifying the complaints of rubber manufacturers regarding the rapid deterioration of their products in this area. However, oxidant smog is becoming increasingly prevalent in other areas, and unusually high oxidant values have been reported in San

Francisco and San Diego on the Pacific Coast, and in the vicinity of Washington, D. C., as well as other localities[2,3,11].

Notwithstanding its limitations, the cumulative rubber test can serve as an index of air pollution. The method is relatively inexpensive, requires very little attention during exposure and lends itself especially to extensive area surveys where climatological conditions are similar. When extended to a comparison of widely different conditions, and used as a screening procedure for the evaluation of air pollution, temperature correction should be applied, and it is advisable to arrange for control of temperature as well as air flow rate.

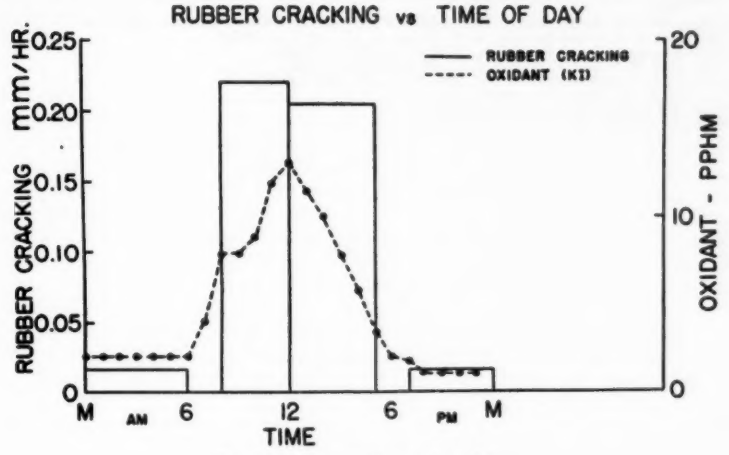

FIG. 6.—Rubber cracking vs. time of day.

The authors gratefully acknowledge the cooperation of the Los Angeles County Air Pollution Control District in supplying the data for ozone maxima during the year 1958, and the hourly oxidant average for the period April 21–26, 1958.

SUMMARY

Cracking of rubber, due to the presence of ozone, was determined in the Los Angeles area by measuring the number of cracks and the crack depth after exposure of standardized bent rubber strips to the atmosphere. The cracking shows a daily and seasonal variation due to the difference in ozone concentration as well as difference in temperature. Results over a three year test period are presented, as well as a comparison with oxidant and ozone values measured in the same area.

The ozone concentration usually reaches a maximum during the day and is highest during the summer months. Its origin has been traced to the action of sunlight on mixtures of organic material and oxides of nitrogen, common air pollutants in urban areas. A comparison with chemical measurements of the oxidizing power of the air shows a similar trend.

The rubber test is useful in the correct interpretation of outdoor exposure tests of rubber goods, since it integrates the variable action of ozone due to large

fluctuations in its concentration and the reaction rate due to climatological factors.

The application of the test to area surveys in air pollution studies is suggested.

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WEATHER AGING OF ELASTOMERS ON MILITARY VEHICLES *

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It is the purpose of this paper to discuss and report on the results of three years of weather aging of rubber items in the high ozone area of Pasadena, California[1].

BACKGROUND

Prevention of ozone cracking of rubber vulcanizates is one of the more serious and important problems of rubber technology. It is also a problem with which the Ordnance Corps has been vitally concerned during the past eight years. Although the cracking of rubber has long been recognized, it was not until after World War II that large scale storage of military vehicles again demonstrated the deleterious effect of atmospheric ozone on rubber. During this period, numerous reports were received from depots throughout the United States describing the severe deterioration of rubber components stored on military vehicles. In order to insure national security and to prevent waste and financial loss by the arbitrary disposal of all questionable material, Ordnance Corps instituted a development program aimed at improving the ozone resistance of synthetic elastomers, thereby increasing serviceability and storage life of all rubber components used by the Military. In cooperation with the rubber industry, Ordnance Corps actively pursued investigations which eventually culminated in the development of ozone inhibitors or antiozonants capable of protecting synthetic rubber vulcanizates against deterioration.

WORK LEADING TO THE PASADENA TESTS

Ordnance Tank-Automotive Command, faced with the reports of field failures, turned to antiozonant development for a solution to the deterioration of tank and automotive end items. A series of contracts were let with Burke Research Co., to find a feasible production antiozonant for SBR items, end item development contracts were let with Mansfield Tire & Rubber Co., Cooper Tire & Rubber Co., Denman Manufacturing Co., and Firestone Tire & Rubber Co., to develop the technology of building ozone resistant tires. Similar contracts, including both tire and automotive mechanical rubber goods, were let with Lee Rubber & Tire Corp., and Dayton Rubber Co. The results were coordinated with industry and tire advisory committees.

While work was going on to develop an antiozonant additive for current production, considerable effort was also concentrated on the preservation of tires, already in storage, by application of protective coatings.

OZONE EXPOSURE TESTS AT PASADENA

Information available indicated that the Los Angeles, California basin had the worst ozone environment, particularly during the smog season and would

* The opinions expressed or contained herein are not to be construed as official or reflecting the views of the Department of the Army. An original contribution presented at the Los Angeles meeting of the Division of Rubber Chemistry, ACS, May 14, 1959.

be an ideal test site, especially since valuable ozone data wa being furnished by air pollution agencies. A composite graph (Figure 1) shows the average ozone concentrations for the three year period. It is interesting to note the gradual drop in ozone concentration each year reflecting the efforts of air pollution agencies to reduce smog and ozone concentrations in the Los Angeles Area.

The majority of the end items were mounted on two trucks in their normal applications[2]. Selected new standard production rubber items were provided from the assembly line of one of the 2½ ton tactical truck manufacturers. Experimental counterparts in various types and degrees of protection were obtained from the experimental contracts and others. Control tires were obtained from some on hand. The standard production line items were mounted on one

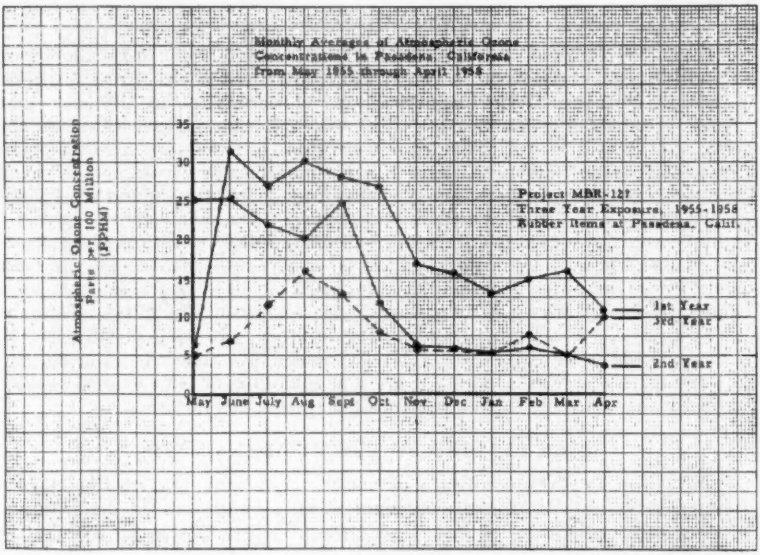

FIG. 1.

2½ ton, 6 × 6, M34 truck, and the experimental items on an identical truck. All parts were photographed at this time. After the installation was completed at the Detroit Arsenal Test Operation Site, Camp Bullis, San Antonio, Texas, the trucks were driven overland to the Los Angeles Ordnance District, Pasadena, California, where they were placed on exposure and re-photographed 18 May 1955. The items, at first, were inspected each week and later each month. Items showing any significant changes were photographed and included in the monthly reports. The crack ratings were indicated as follows:

No cracking	0
Very slight cracking	1
Slightly cracked	2
Cracked	3
Badly cracked	4
Very badly cracked	5
Failed	6

Since SBR is the most widely used synthetic elastomer in military applications, considerable effort was directed toward the compounding of this material for improved ozone resistance. The concurrent development of improved methods of accelerated ozone testing greatly facilitated the task of screening

FIG. 2.—Tire flap mounted in wheel assembly and exposed for one year at Pasadena, California. Cracking was most pronounced in valve slot area. (Code 14 A-1.)

various types of antiozonants. The results of preliminary evaluation indicated that antiozonants when at levels of 3 parts of dioctyl-*p*-phenylenediamine in combination with 1 to 2 parts wax, per 100 parts RHC would provide adequate protection for SBR in many applications.

The use of improved types of antiozonants, with suitable waxes, has proven to give satisfactory protection for one year or longer against ozone cracking

after exposure to the high ozone atmosphere at Pasadena, California. As a result, the present military specification for tires (MIL-T-12459A) requires that new tires manifest ozone resistance comparable to Ordnance Controls containing 2 parts Santoflex AW, 2 parts of UOP-88, and 1.5 parts Atlantic No. 1115 wax per 100 RHC. In addition, ozone resistance is called for on many Ordnance mechanical rubber items, referenced by Suffix C_1 of specifications MIL-R-3065 and MIL-STD-417.

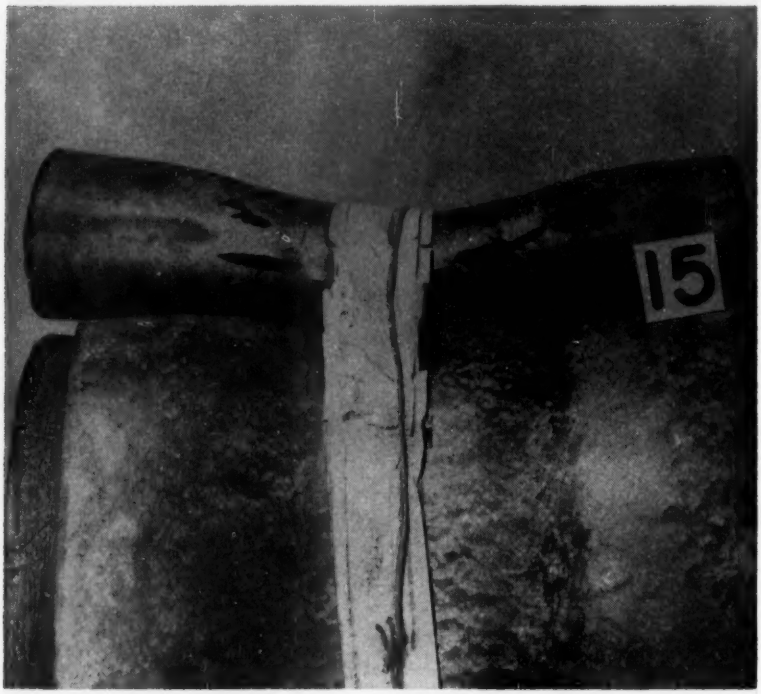

FIG. 3.—Tire flap exposed for one year at Pasadena, California. Cracking was most pronounced in creased areas. (Code 15.)

In addition to conducting exposure tests at Los Angeles, identical items were also exposed at other test sites. These sites included the Detroit Arsenal; Yuma, Arizona; Philadelphia, Pennsylvania; Dayton, Ohio; San Antonio, Texas; Fort Greeley, Alaska; and Fort Churchill, Canada.

In comparing the degree of cracking of like items in Los Angeles area and the other parts of the country, it is estimated that one year of exposure in Los Angeles is equivalent to approximately 3–5 years in other areas where the average ozone concentration is between 3 to 10 pphm as compared to 10 to 66 pphm in the Los Angeles basin. Due to the fact that the antiozonants gradually migrate to the surface and are consumed in 3–5 years, a definite limitation is placed on the period of ozone protection afforded by the antiozonants com-

pounded into the rubber. Therefore, if tires or other rubber items in storage are to be protected beyond this period, it may be necessary to surface coat them with an antiozonant such as a 50–50 mixture (by volume) of dioctyl-*p*-phenylenediamine (MIL-D-50000) and acetone.

DISCUSSION OF RESULTS

SBR Test items.—Test items such as weather strips, weather seals, and rear axle bumpers showed no evidence of cracking when protected with 3 parts of a dioctyl-*p*-phenylenediamine type antiozonant plus 1 to 5 parts of wax. The

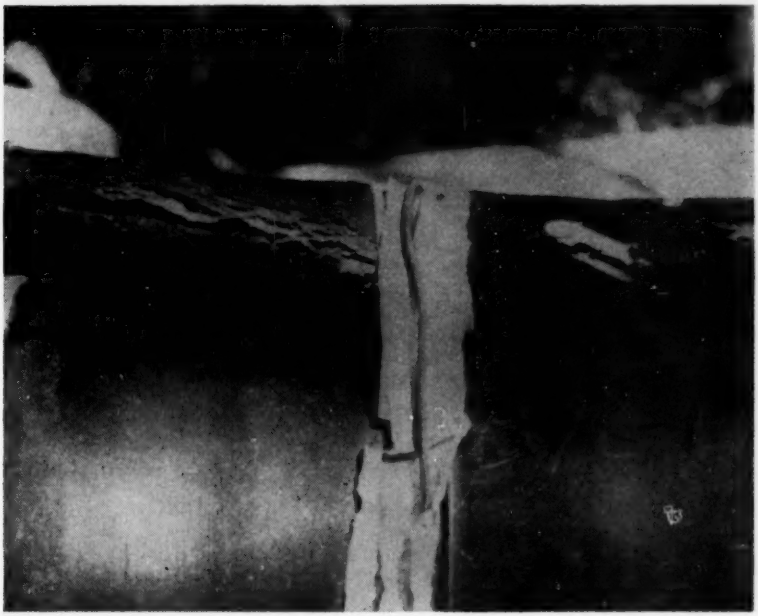

FIG. 4.

controls, on the other hand, were rather severely deteriorated. It is interesting to note that door weather seals composed of natural rubber sponge with a skin coating of SBR, with antiozonant and wax exhibited severe cracking. Since the natural rubber was unprotected, the antiozonant apparently migrated preferentially into the sponge, thereby causing a deficiency of protectant at the surface. These results indicate the necessity of dispersing the antiozonant uniformly throughout the rubber to ensure adequate protection.

In the case of tire flaps mounted on wheel assemblies, ozone cracking was most severe around the valve slot (Figure 2, Code 14A-1), the only area directly exposed to the atmosphere. Flaps stored in the rolled up position (Figure 3, Code 15), exhibit the most cracking in the creased area where stresses are the greatest. Results indicate that SBR flaps exposed in the rolled-up position are

difficult to protect. This is also true when naturally ozone resistant butyl flaps are used (Figure 4, Code 37Cl).

Tires (*SBR*).—The results of exposure and weathering test has demonstrated that SBR tires may be adequately protected by the incorporation of 3

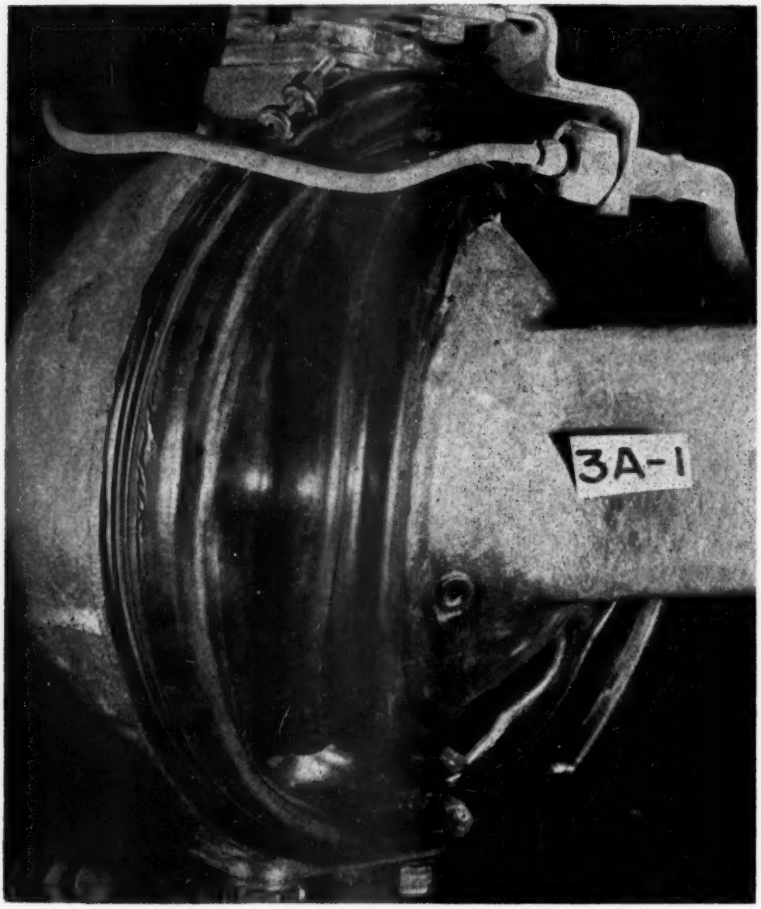

FIG. 5.—Front axle boot composed of nitrile rubber. Item was exposed for one year at Pasadena, California. (Code 3A-1.)

parts of antiozonant such as dioctyl-*p*-phenylenediamine and phenyl cyclohexyl-*p*-phenylenediamine types, with 1 part of suitable wax. Tires thus protected and mounted on military vehicles and exposed at Pasadena showed no cracking in one year and in many instances no cracking was indicated for two years. It was interesting to note that tires which were crack-free for two years

were suddenly cracked at the end of this period. This indicates that once the antiozonant is depleted through migration to the surface, the tire will fail as quickly as the controls. In most cases, SBR controls containing no antiozonant, cracked badly within the 2nd or 3rd week of exposure. Another inter-

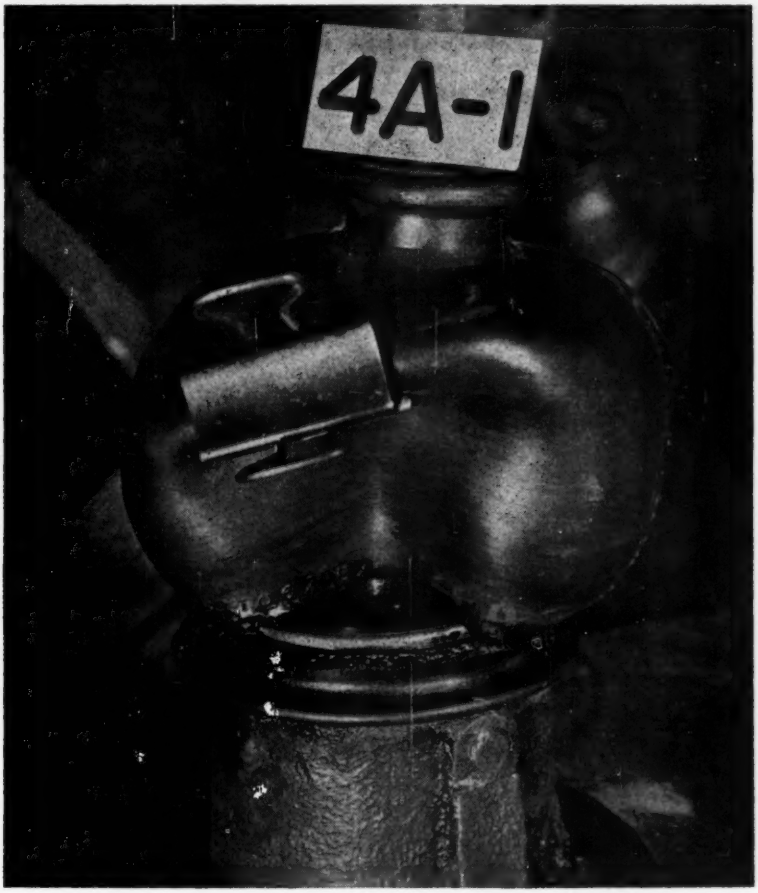

FIG. 6. Shift lever grommet composed of nitrile rubber. Item was exposed for one year at Pasadena, California. (Code 4A-1.)

esting observation was the fact that the cracks which develop on the shaded side of the tire are fewer in number but larger and deeper than those appearing on the sides exposed to sunlight. Apparently, direct exposure to sunlight produces the necessary temperature gradient to ensure continuous migration of antiozonant to the surface and thus effects a noticeable reduction in the severity of cracking.

Nitrile rubber test items.—From results of exposure testing, it is evident that nitrile rubbers are notably poor in ozone resistance. The addition of 3 parts dioctyl-*p*-phenylenediamine with 1 part of wax added to a nitrile stock plasticized for low temperature applications, did not give satisfactory protection and failed completely before 12 months. (Figure 5, Code 3A1) shows a front axle boot after 12 months. Similar bad results were obtained with the shift lever grommet (Figure 6, Code 4A1). However, when the nitrile rubber was com-

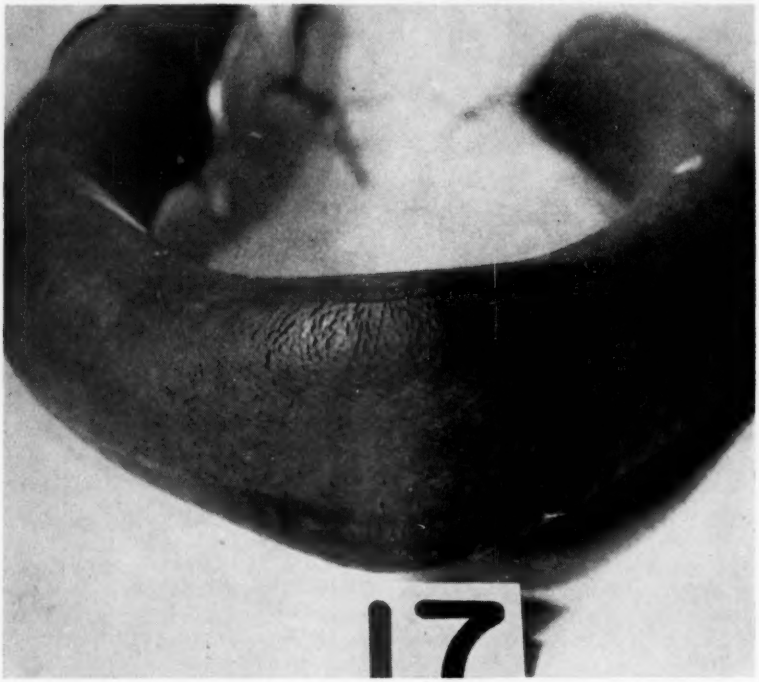

FIG. 7.—Neoprene covered hose exposed for one year at Pasadena, California. (Code 17.)

pounded with 4 parts of nickel dibutyldithiocarbamate and 1 part of wax, the shift lever grommet installed in the normal position was still crackfree at the end of 31 months of exposure (Code 4B1).

Neoprene (polychloroprene) rubber test items.—That neoprene is noticeably resistant to weathering and ozone attack is now well established. However, the term "neoprene" is not a magical word connoting ozone resistance. Unless the polymer is properly compounded, its excellent weathering properties are not apparent.

The results of exposure testing at Pasadena indicate that neoprene can be compounded to give satisfactory ozone resistance. A neoprene covered hose of unknown composition (Figure 7, Code 17), developed its first cracks in 72

days. However, it should be noted that this item was exposed under conditions of high stress and the cracking did not appear to progress.

Butyl rubber test items.—Resistance to ozone attack is one of the unique properties of butyl rubber. But here again, like neoprene, it must be properly compounded to retain its inherent ozone resistance.

The use of high plasticizer levels to meet the low temperature requirements of rubber items on military vehicles results in lowering of the ozone resistance, which can be regained by the addition of suitable antiozonants. In this respect, butyl shows no advantage over SBR when both are protected by anti-

FIG. 8.

ozonants. And in the case of butyl rubber versus SBR rubber containing an antiozonant, SBR shows greater ozone resistance. Figure 8 (Codes 30B and 31B) shows a highly plasticized and ozone protected butyl windshield wiper hose and an ozone protected SBR windshield wiper hose. The superior ozone resistance of ozone protected SBR base over ozone protected butyl hose is again indicated. The photograph was taken after two (2) years exposure. The butyl hose was very badly cracked at 12 months, whereas, the SBR hose still shows no cracks after 31 months exposure.

Polyurethane test items.—Polyurethane rubbers, which are relatively new, promise to have many uses for end items used on military vehicles. Its excellent oil, ozone and tear resistance in addition to its high tensile strength makes it ideal for many mechanical rubber items. A front axle boot made from this material was placed on a vehicle and tested at Yuma, Arizona, without failure.

A duplicate boot (Code 6C) has been stressed and exposed at Pasadena and no sign of ozone cracking has appeared at the end of the 20th month of exposure.

Protective coatings.—Before current practice of incorporating the antiozonant in the rubber compound became commercially feasible, considerable effort was concentrated on the preservation of tires by the application of protective coatings. Although this method is costly and time consuming, development was pursued because of the need of preventing further cracking of unprotected tires currently in storage. Investigation of a number of vinyl, neoprene, and hypalon base coatings were made at Detroit Arsenal. The ease of application, drying time, film adhesives, etc., were evaluated by spraying and brushing the

FIG. 9.—Protective coatings applied to tires showing examples of blistering, peeling and cracking. Tires were exposed for several years at Detroit Arsenal.

coatings on standard size 9.00–20 military tires. After the films had dried, the tires were mounted on wheels and inflated to 45 psi. They were then placed on test racks at a 45 degree angle with the upper surface of the tire facing directly to the South.

The test results obtained over a period of several years outdoor exposure indicate that these protective coatings, applied either by spraying, or brushing, are subject to cracking, peeling, blistering, and pin-holing[3]. The weathering of various types of these coatings applied to tires, exposed for 2 or 3 years at Detroit Arsenal is illustrated in Figure 9. The film failures were apparent in every case. The use of coating was indorsed only as a temporary expedient for preservation of unprotected tires currently in storage. However, at a January 1959 Wheeled Vehicle Processing Conference held at Detroit Arsenal, a decision was reached to recommend the elimination of application of surface

coatings to unprotected tires in storage unless it can be proven that the savings in increased serviceability is greater than the cost of preservation. If no savings are indicated, it is entirely possible that Ordnance will eliminate the preservation of tires by surface coating and rely entirely on the protection given by the addition of antiozonants to the rubber compounds.

A possible material that might be considered for future use in coating unprotected military tires in storage is a 50/50 mixture (by volume) of dioctyl-*p*-phenylenediamine and acetone. Tires coated with a dip coat of this mixture

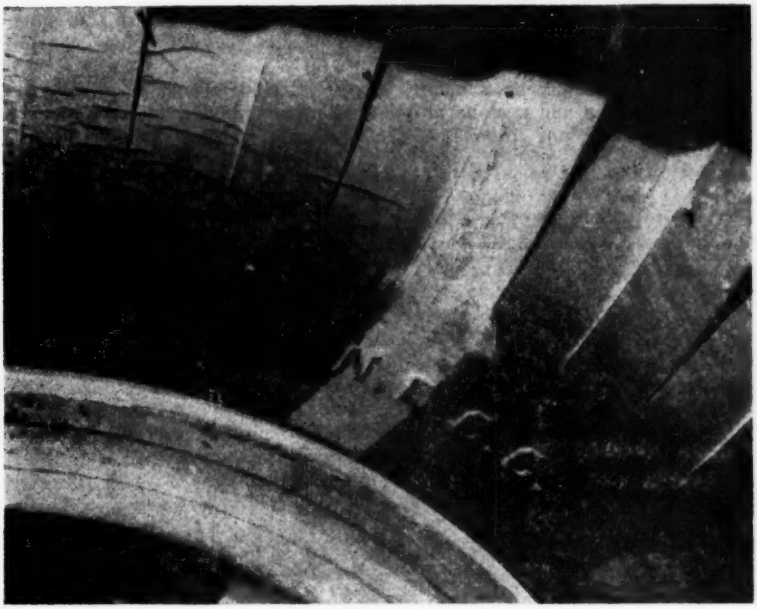

FIG. 10.

were crack-free for 17 months when exposed to the Pasadena atmosphere. Cracking appeared in the 18th month. This result is comparable to results obtained when 3 parts of the same antiozonant with 1 part of a suitable wax is added to the basic rubber recipe. A tire coated with this mixture is shown in Figure 10 (Code 18Cl) at the end of 12 months. The cracked portion is that of the control section which was badly cracked.

One point that should be emphasized is that the use of this or any other surface coating is only recommended for the protection of tires that do not contain an antiozonant in its recipe and are on stored vehicles. The most satisfactory method of protecting tires and other mechanical rubber items against ozone attack is to incorporate suitable antiozonants and wax into the compound at the time of manufacture.

CONCLUSIONS

The results of the Ordnance Corps Pasadena exposure tests may be summarized as follows:

1. The ozone resistance of synthetic elastomers, particularly SBR, can be substantially improved by the addition of suitable antiozonants and waxes to the rubber compound.

2. The one to two years protection at Pasadena appears to be equivalent to 3–5 years protection in other areas where ozone concentrations are low.

3. Butyl and neoprene rubbers which have inherent high ozone resistance become less effective when plasticized to meet the military's low temperature requirements and require the addition of suitable antiozonants and careful compounding in order to regain their ozone resistance.

4. Polyurethane rubbers promise to play an important role in the manufacture of many end items used on military vehicles when it becomes economically available.

5. For storage purposes a surface coating with a 50/50 mixture of dioctyl-*p*-phenylenediamine and acetone promises to impart good ozone resistance to tires that were not protected against ozone during manufacture.

REFERENCES

[1] Data supplied by Jan W. Haagen-Smit, under Contract No. DA-04-495-ORD-886 (Report No. 61, 3rd exposure year) initiated by OTAC, Detroit Arsenal, June 1958.
[2] Detroit Arsenal Test Operation, Project MBR-127 conducted under Contract No. DA-04-200-ORD-475 with Wetmore Hodges and Associates, Inc., Camp Bullis, Texas.
[3] Detroit Arsenal Laboratory Report No. 2865 dated 24 March 1954.

CHEMICAL INHIBITION OF OZONE DEGRADATION OF SBR *

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INTRODUCTION

The reaction of ozone with rubber was shown by Harries[1] to effect rapid chain scission and severe degradation of an unsaturated polymeric structure. Other early researchers were able to show that ozone attacks vulcanized rubber[2,3,4,5] while Van Rossem[6] made substantial contributions toward identification of the conditions for ozone attack. It was shown by Van Rossem that ozone attack is a surface phenomenon of stretched rubber with the most rapid cracking occurring at 10–20% elongation. The very interesting conclusion was made that the cracking of rubber by the attack of ozone was to be regarded as a typical property of stretched rubber. In the light of the technology of antioxidants and protective agents of that day, the observation by Van Rossem was quite logical, and the recognition of ozone attack as a surface reaction stimulated the search for materials which would serve as a physical barrier to ozone attack. As late as 1951 the rubber literature still contained observations that no chemical protective agents were known but only protective barriers such as waxes were effective in inhibiting the attack of ozone on stressed rubber[7]. Newton[8] and Crabtree and Kemp[9,10] proved conclusively the deleterious effect of ozone on rubber and they established the conditions under which ozone degradation is most severe.

Many excellent reviews[11,12] of the status of ozone technology and descriptions of active compounds[13,14] have been published recently. While chemical and physical additives are known which will prevent the deterioration of rubber in an ozone-rich atmosphere, it must still be concluded that the mechanism of cracking of stressed rubber is not known in detail.

Variations in structures of active compounds involving substitution of electropositive and electronegative groups can be made which effect significant changes in activity. Steric influences can be illustrated by comparing polysubstituted derivatives. Some of the chemical structure/antiozone activity relationships will be described in detail. All comparative evaluations have been carried out in SBR in this study. Unprotected SBR can be shown to crack more rapidly than natural rubber in an ozone atmosphere, so studies were made with a single elastomer for simplicity in the laboratory manipulations.

EXPERIMENTAL

The apparatus and methods used to assess the antiozonant effectiveness of the chemical additives were essentially those described in the publication by Creed, Hill and Breed[13]. The test specimen was a molded circular belt measur-

* An original contribution. Presented at the Los Angeles meeting of The Division of Rubber Chemistry, ACS, May 14, 1959.

ing ½ inch wide, ¼ inch thick, and $5\frac{5}{16}$ inches in diameter. Ozone was generated by a Hanovia burner (0), and the concentration was maintained at 25 ± 5 pphm (parts per 100,000,000) in the test chamber. The ozone concentration was determined twice daily, once by the conventional KI method of Crabtree and Kemp[10] and secondly by the method of Beatty and Juve[15]. Under normal operating conditions the two methods gave excellent agreement of the ozone concentration.

The circular test specimens were supported on a series of one inch, rotating stainless steel rods which were actuated by a series of gears outside of the test chamber. The rods were rotated, and as any section of the test specimen passed over the roll, a momentary elongation through a range of 0 to 20% was provided. A flexing rate of seventy-five flexes per minute was maintained. Normal operating temperatures in the ozone cabinet were 35°–40° C.

TABLE I

CONCENTRATION OF PROTECTIVE AGENT AND OZONE RATING

phr of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	Ozone rating
0.0	25
0.5	65
0.75	80
1.0	95
1.5	100
2.0	120
2.5	130
3.0	135

The degree of cracking of the test specimen was measured using the visual comparison system of assigning rating numbers of 1 to 6 as compared to a standard reference. The number 1 was assigned to a stock as long as there were no visible cracks and the number 2–6 were assigned to increasing severity of ozone attack. An unprotected SBR tread formulation would normally crack to a 6 rating after 24 to 48 hours exposure in the test chamber. Test specimens were visually compared twice daily and an appropriate number rating assigned.

A formula for calculating the ozone rating was devised:

$$A = 7n - \sum_{1 \to n} r + \frac{r_n - 1}{2}$$

A = absolute ozone rating
n = number of individual observed ratings
r = numerical value of the observed rating

$$\frac{A_{\text{experimental}}}{A_{\text{control}}} \times 100 = \text{ozone rating}$$

This formula, a modification of the method of Creed, Hill and Breed[12], involves fewer arithmetic calculations, and essentially identical ratings are obtained within experimental error of the overall methods.

In all subsequent data the arbitrary rating of 100 is assigned to the degree of protection afforded by 1.5 phr of 6-ethoxy-1,2-dihydro-2,2,4-trimethyl-

TABLE II

TEST FORMULATION

SBR 1502[a]	100.0
Philblack O[b]	50.0
Zinc oxide	4.0
Stearic acid	2.0
Para flux[c]	10.0
Sulfur	1.75
Santocure NS[d]	1.2
Antiozonant	1.5

Test specimens were cured 60 min @ 144° C.
[a] American Synthetic Rubber Corp.
[b] Registered Trademark—Phillips Petroleum Co.
[c] Registered Trademark—C. P. Hall Co.
[d] Registered Trademark—Monsanto Chemical Co.

quinoline, and all other ozone ratings are relative to this degree of ozone protection. Test additives are compared on an equal weight basis of 1.5 phr.

As shown in Table I the degree of antiozonant protection is a function of the concentration of the chemical protective agent. The relative ozone resistance of the formulation increases as larger quantities of active material are used.

Test compositions were compounded, milled and cured in accordance with procedures given in ASTM D15-54T[16]. The compound formulation is given in Table II. A nonstaining grade of SBR which contained no amine antioxidant was used in order to avoid any possible masking or synergistic interactions between the amine types of antidegradants.

RESULTS

The observation of Gaughan[17] that "conventional antioxidants give protection against ozone cracking mostly by accident" is essentially true. A comparison of several chemical types of "conventional" rubber antioxidants is shown in Table III. The compounds in Table III which are known to impart a high level of protection to SBR against attack by ozone are of two basic types: (a) N,N′-disubstituted *para*-phenylenediamines and (b) 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. Compounds in these two classes were known to be antioxidants for rubber before the antiozonant activity was recognized.

TABLE III

COMPARISON OF STANDARD ANTIOXIDANT TYPES

Antioxidant	Ozone rating
None	25
6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	100
4,4′-Thiobis(6-*tert*-butyl-*m*-cresol)	25
p,p′-Di-*tert*-octyldiphenylamine	25
2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)	25
2-Mercaptobenzimidazole	25
N-Phenyl-2-naphthylamine	40
Diphenylamine/acetone condensate	50
Diphenylethylene diamine	50
Polymerized 1,2-dihydro-2,2,4-trimethylquinoline	60
Wing-Stay 100[a]	100
N,N′-Di-*sec*-octyl paraphenylenediamine	115
N-Cyclohexyl-N′-phenyl-*p*-phenylenediamine	115

[a] Registered Trademark—Goodyear Tire & Rubber Co.

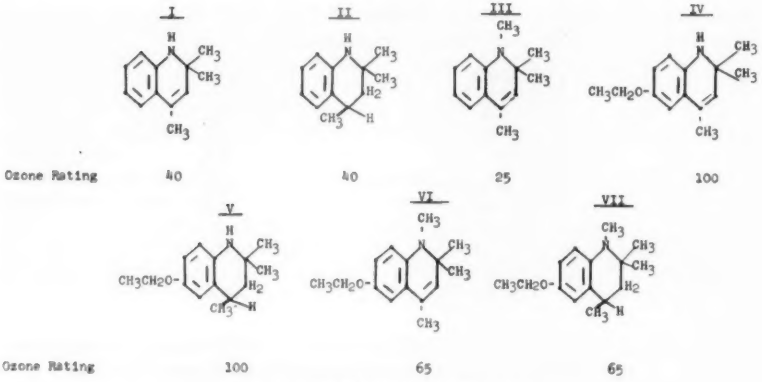


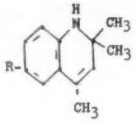
FIG. 1.—Comparison of quinoline structures.

A systematic synthesis program was initiated to determine what substituents are important in imparting antiozone activity to a known antioxidant structure. A marked difference in antiozone activity was observed between the 6-ethoxy and the unsubstituted 1,2-dihydro-2,2,4-trimethylquinoline, while little change in antioxidant effectiveness was measured. The 1,2-dihydro-2,2,4-trimethylquinoline structure was chosen for variations in the chemical substitutions.

The first modifications in the structure are shown in Figure 1. The comparison shows the 6-ethoxy group (IV) to be necessary for antiozone activity.

TABLE IV

VARIATIONS IN 6-SUBSTITUTED DERIVATIVES



R	Ozone rating
H—	40
CH_3O—	85
CH_3CH_2O—	100
	95
$(CH_3)_2CH$—	65
$(CH_3)_3CCH_2$—	70
$(CH_3)_3C$—	65
	50
$C_{12}H_{25}$—	65
$CH_3(CH_2)_3CH_2$—	60

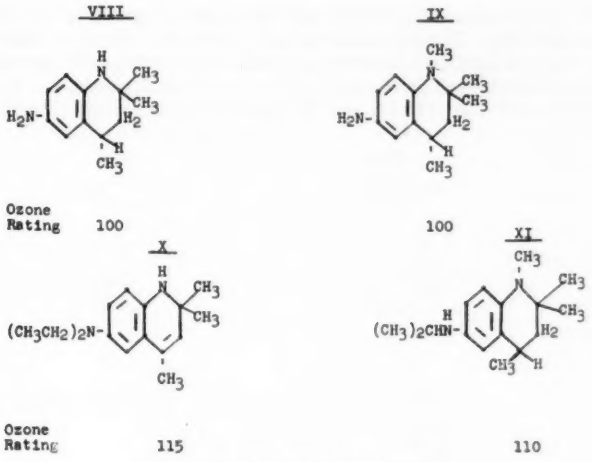


FIG. 2.—6-Amino substituted quinolines.

Hydrogenation of the 3,4-double bond (V) had no effect on the antiozone activity. The reduced derivative was as effective as the parent compound. However, when the hydrogen atom on the secondary amine group was replaced by a methyl group (VI), the antiozone effectiveness was greatly reduced.

In order to determine the influence on antiozone activity of variations in the 6-substituent of the quinoline series, the derivatives shown in Table IV were prepared. The alkoxy substituents were shown to retain a high level of antiozone activity, while alkyl substituents of the *tert*-butyl, *tert*-amyl, or dodecyl type, which are known to be much less electropositive, had little or no beneficial effect on the antiozone activity.

The effect on antiozone activity of substituting strongly electropositive groups in the 6-position of the 1,2-dihydro-2,3,4-trimethylquinoline is shown in

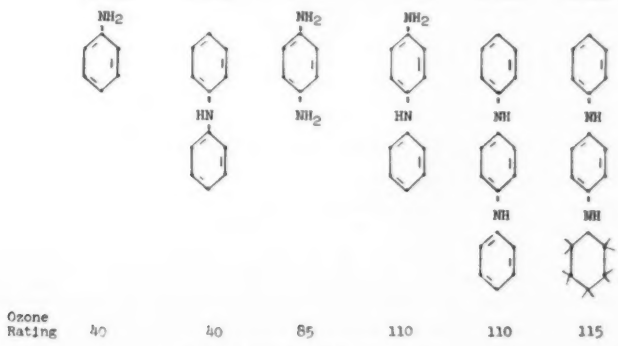


FIG. 3.—Aromatic amine comparisons.

Figure 2. The amino, alkylamino, and dialkylamino group all contribute to antiozone activity. The alkylamino group is known to be much more electropositive than the alkyl or alkoxy group, and it can be observed that antiozone effectiveness increases as the basicity of the quinoline is increased. A comparison of compound III, VI, IX and XI shows that the ring nitrogen can be

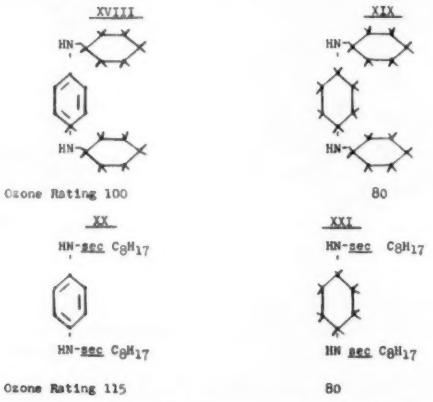


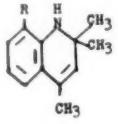
FIG. 4.—Comparison of hydrogenated *para* phenylenediamines.

alkylated without loss of activity if a primary or secondary amine group is present in the 6-position.

The substituted aromatic system which is necessary for high levels of antiozone activity in the quinoline series is further illustreated in the *para* phenylenediamine system. Aniline and diphenylamine exhibit little or no activity as

TABLE V

8-SUBSTITUTED QUINOLINES



R	Ozone rating
CH_3—	50
CH_3O—	40
CH_3CH_2O—	50
$CH_3(CH_2)_3CH_2O$—	55
$CH_3(CH_2)_3CH_2$—	50

antiozonants in SBR. However, as shown in Figure 3, when amino, alkylamino, or arylamino groups are substituted in the *para* position, high levels of antiozone effectiveness are obtained. When the conjugated aromatic system is removed by hydrogenation, the antiozone activity is greatly reduced as shown in Figure 4.

When the 8-substituted quinolines shown in Table V were prepared and tested, none of the derivatives was found to exhibit significant antiozone effectiveness. The 8-methyl derivative was not expected to show any significant activity, but the low activity of the 8-ethoxy-1,2-dihydro-2,2,4-trimethyl quinoline was somewhat surprising. The change of the ethoxy group from the 6- to the 8-position should have a minor effect on the mesomeric

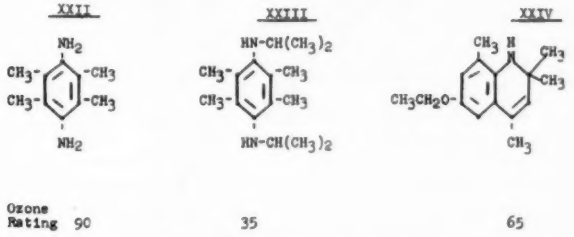


FIG. 5.—Sterically hindered amines.

character of the group but significant changes in the steric character of the molecule might be expected. The 1,2-dithydro-2,2,4-trimethyl quinoline compund is basically a hindered amine structure, and the substitution of one additional group in the 8-position seriously reduces the reactivity of the secondary amine.

An additional example of the steric influence is illustrated in Figure 5. When the sterically hindered *para*-phenylenediamine (XXII) is dialkylated

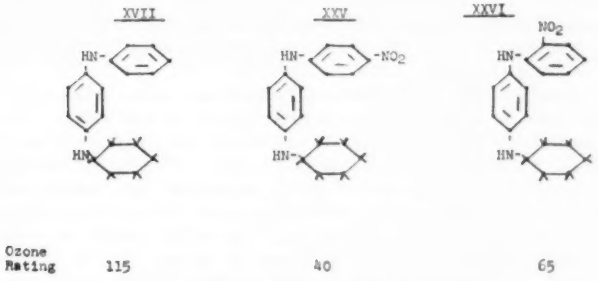


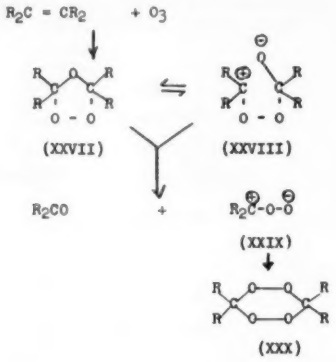
FIG. 6.—Nitro substituted *para* phenylenediamines.

(XXIII), antiozone activity is lost. Substitution of a methyl group in the 8-position (XXIV) of an active compound greatly reduces the antiozone activity.

The decrease in antiozone effectiveness which is produced by the substitution of an electronegative substituent is illustrated in Figure 6. Nitro groups in the *para*- (XXV) and *ortho*- (XXVI) positions have a large negative influence on the antiozonant activity.

DISCUSSION

The reaction of ozone with an aliphatic double bond has been shown to proceed through the following sequence of reactions[18]:



The result of this series of reactions can be readily seen as leading to chain scission and a reduction of effective molecular weight of a polymeric system. However, the severe degradation of SBR during exposure to ozone cannot be explained solely on the stoichiometry of the above reactions. The relative instability of molecular species of types such as (XXX), (XXIX), and (XXVII) has long been recognized, and it is concluded that the severe degradation is due to the formation of radicals which can initiate additional degradation reactions. Ozone degradation is therefore postulated to be an ozone-induced free radical chain reaction of a very rapid and complex type. The observations[11] that antiozonants function by stoichiometry rather than chain stopping could perhaps be modified to read that antiozonants function by stoichiometry *in addition to* chain stopping.

The observed differences between antioxidant and antiozonant types in Table III may be attributed to relative degrees of reactivity. Since ozone attack normally is studied at room temperature, only the more reactive compounds will be capable of operating effectively. It is recognized that ozone attack is a surface reaction, and solubility, migration, and volatility characteristics become very important in controlling ozone induced degradation. The basic strength and steric requirements of an amine would be important if adducts with (XXVIII) and (XXIX) are to occur. In the comparison of 6-substituted 1,2-dihydro-2,2,4-trimethylquinolines the mesomeric effect of the alkoxy and alkylamino groups in compounds IV and X is illustrated with high levels of antiozone effectiveness. When resonance stabilization is prevented by hydrogenation of the aromatic systems, lower levels of antiozone activity are observed as shown in Figure 4. Based on the results obtained in this study the following conclusions can be made:

1. Chemical additives can impart a high level of antiozonant protection to flexing SBR vulcanizates.

2. Electropositive substitution of the aromatic amine system is necessary for high levels of antiozonant activity in SBR.

3. Ozone resistance of SBR vulcanizates is improved with increasing concentrations of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.

4. The substitution of electropositive groups in the 6-position of the 1,2-dihydro-2,2,4-trimethylquinoline imparts a high level of antiozonant activity.

5. The substitution of electronegative groups in an active structure reduces antiozonant activity.

6. Steric hindrance and resonance influences are important in altering the activity of an antiozonant.

SUMMARY

The standard rubber antioxidant types which are capable of imparting ozone resistance to SBR vulcanizates are summarized. The 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and *para* phenylenediamines are shown to represent the most active structures. Steric, mesomeric, and resonance effects are shown to be important in imparting high levels of antiozone activity. When electronegative groups are substituted in an active structure, antiozone effectiveness is greatly reduced. Antiozonant activity is attributed to efficient stopping of ozone-induced free radical chain reactions in the polymeric structure.

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THE EFFECT OF CARBON BLACK ON THERMAL ANTIOXIDANTS FOR POLYETHYLENE *

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INTRODUCTION

Oxidation of polyethylene, which results eventually in physical and dielectric failure of the polymer, is caused by heat and ultraviolet radiation. Photo-oxidation is practically stopped by the addition of 3% by weight of fine particle size carbon blacks[1] which also act under accelerated test conditions as mild thermal antioxidants. Small amounts of organic inhibitors, which are stronger high temperature antioxidants than carbon black, are customarily added to polyethylene to provide additional thermal protection during processing and subsequent exposure. In many instances carbon black and a conventional amine or phenol antioxidant are added together to protect polyethylene against both thermal and photo-oxidation. Though it effectively protects against photo-oxidation, carbon black reduces the activity of many thermal antioxidants, rendering several completely ineffective.

EXPERIMENTAL METHODS

The polyethylene used for all oxidation tests was taken from a single batch of high pressure, high molecular weight polymer of 0.92 density. The carbon black was an acidic channel black having an average particle diameter of 120–180 A. The antioxidants used were commercial samples.

Mixtures of polyethylene with carbon black and/or antioxidant were prepared by mill massing on a 6-inch by 12-inch, 2-roll mill having roll speeds of approximately 25 to 35 rpm with the rolls at a temperature of 120° C (250 ± 5° F). A master batch of antioxidant in polyethylene was prepared and then cut back to the desired antioxidant concentration. Mixtures containing carbon black were prepared from a 25% master batch of carbon black in the polyethylene described above. This procedure insured optimum dispersion of the carbon black.

Oxidation rates were determined by an accelerated test in which the amount of oxygen reacting with the sample was measured volumetrically. All data reported herein are the result of measurements made at 140° C in the apparatus shown in Figure 1. A detailed study of these reactions over a temperature range extending down to 80° C is in progress and will be reported later.

Reaction vessels consisted of 14-inch lengths of 8-mm o.d. Pyrex tubing sealed at one end. Enough Type 4A Linde Molecular Sieve, a synthetic zeolite, to fill 1 to 1½ inches of the tube was used as an adsorbent for water and carbon dioxide. The adsorbent was held in place by a small plug of glass wool, and 0.1 g of the milled polyethylene sample approximately 50 mils thick was

* Reprinted from the *Journal of Applied Polymer Science*, Vol. 1, pages 37–42 (1959).

then inserted. A second plug of glass wool was placed about 1½ to 2 inches from the open end of the tube, at about the point where the tube was to pass through a hole in the side of the oven. The purpose of this plug was to prevent heat loss and to catch any condensing materials which might otherwise con-

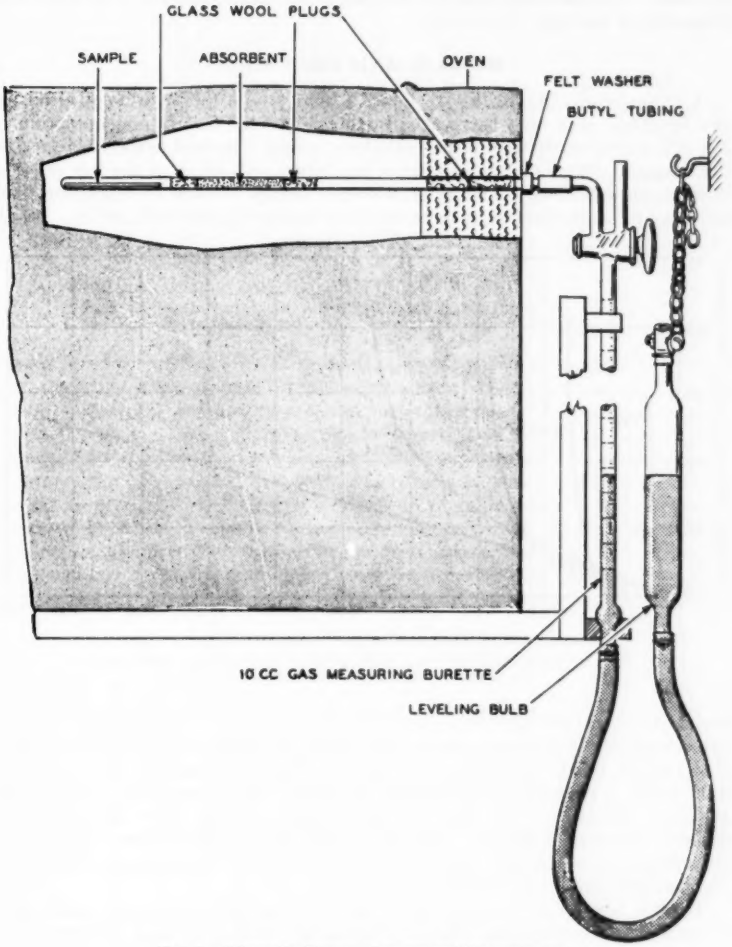

FIG. 1.—Schematic diagram of oxygen uptake apparatus.

taminate the gas buret. The air in the reaction tube was replaced with oxygen by alternate evacuation and refilling with oxygen.

The reaction tubes were placed in an air-circulating oven maintained at 140 ± 0.5° C and immediately connected to gas burets filled with oxygen. After temperature equilibrium was reached, the system was adjusted to atmos-

pheric pressure and an initial reading was made. Oxygen uptake was measured by subsequent readings at atmospheric pressure. Similar tubes containing no polyethylene samples were placed in the oven as blanks to provide a correction for changes due to fluctuating room and oven temperature and atmospheric pressure. All materials were run at least in duplicate, and reaction tubes were discarded at the end of each run.

RESULTS AND DISCUSSION

Carbon black, in addition to being a light screen for ultraviolet radiation, also functions as a mild thermal antioxidant at 140° C. In concentrations of 2 or 3%, customarily used in polyethylene, a well dispersed carbon black in the size range of 500 A or less compares favorably with some of the less effective thermal antioxidants. The amount of protection derived from carbon black increases in proportion to its concentration in the polymer (Figure 2). At the

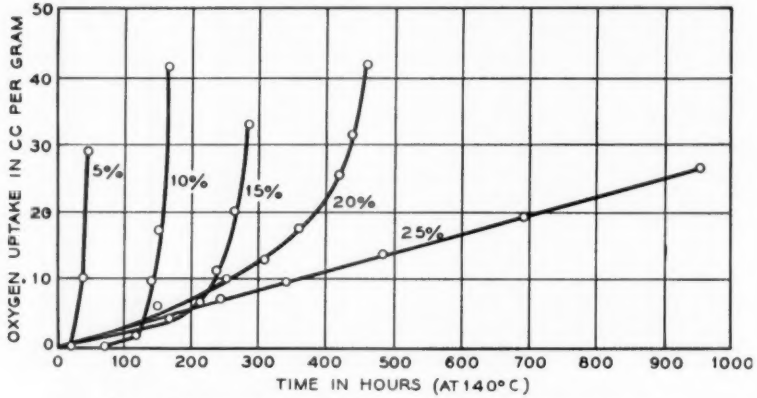

FIG. 2.—Relationship between increasing carbon black concentration and the thermal oxidation rate of polyethylene.

lower concentrations the rate curves are typical of an autocatalytic reaction, but autocatalysis becomes less evident with increasing concentration until at 25% carbon black, oxidation proceeds at a slow, steady rate for a period of 1000 hours. Higher concentrations of carbon black seemingly remove peroxides so effectively that their homolytic cleavage into new, chain-initiating radicals becomes negligible. However, for many polyethylene applications concentrations of carbon black above 5% are believed to have a deleterious effect on physical and dielectric properties.

Carbon black may function as a trap for propagating radicals, or its role as an antioxidant could be due to the presence of a low molecular weight fraction capable of migrating into the polymer. The latter possibility seems unlikely since exhaustive evacuation of carbon black at 200° C does not decrease antioxidant effectiveness. However, reactions which are believed to modify chemical groups on the carbon surface do influence antioxidant behavior[2]. A typical channel black (Figure 3) with 5% "volatile" content* at 3% concen-

* The "volatile" content of carbon black is measured by ASTM Method D 271-48 which removes essentially all of the oxygen containing groups from the carbon surface by pyrolysis.

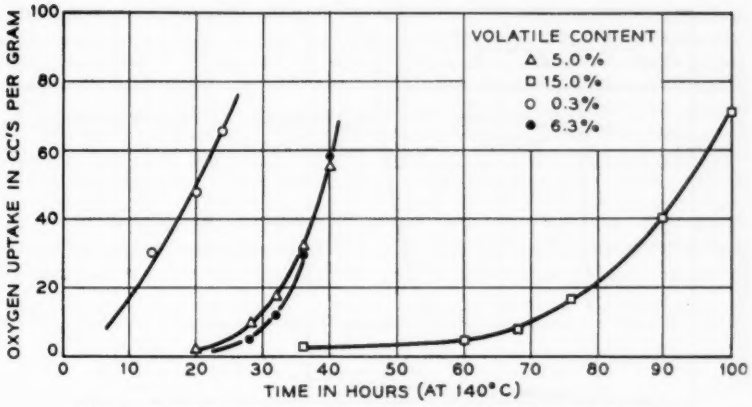

FIG. 3.—Dependence of the thermal oxidation rate of polyethylene containing 3% carbon black on the volatile content of the carbon black.

tration gives about 30 hours of protection to polyethylene at 140° C. When this carbon black is activated by heating in air until the volatile content reaches 15.0%, it becomes a much more effective antioxidant. The process may be reversed by deactivation at high temperature in the absence of oxygen, converting the carbon black to a form (0.3% volatile) which gives no thermal protection. The deactivated form may be partially reactivated to a volatile content of 6.3% by reheating in oxygen. The exact nature of the chemical reactions which occur during these treatments is not known, but the volatile content, as measured by standard techniques, increases as the carbon black is activated and decreases with deactivation. Polarographic and infrared data indicate the presence of a variety of oxygen groupings on the surface of carbon

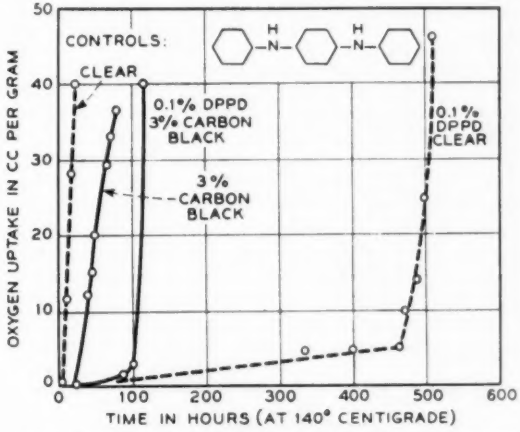

FIG. 4.—Effect of carbon black on the behavior of *N,N'*-diphenyl-*p*-phenylenediamine as an antioxidant in polyethylene.

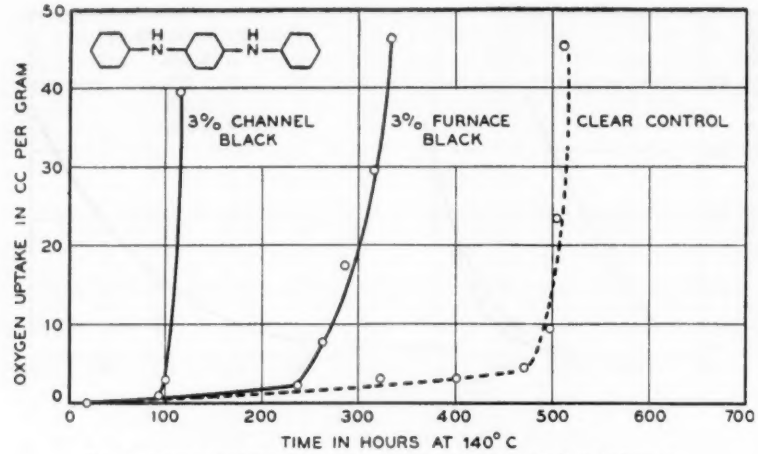

FIG. 5.—Thermal oxidation rate of polyethylene containing 0.1% *N,N'*-diphenyl-*p*-phenylenediamine in the presence of various carbon blacks.

black[3,4]. Presumably the content or nature of such groupings is modified in the cycle of heat treatments. The effect of a wide variety of reactions on the chemical composition of carbon black and the behavior of these modified carbons with various antioxidants is now under way.

Antioxidants which had been developed for the protection of natural rubber were the first to be used as inhibitors for the thermal oxidation of polyethylene. These antioxidants were characteristically amines or phenols containing one or more active hydrogen atoms. Diphenyl-*p*-phenylenediamine, a typical amine

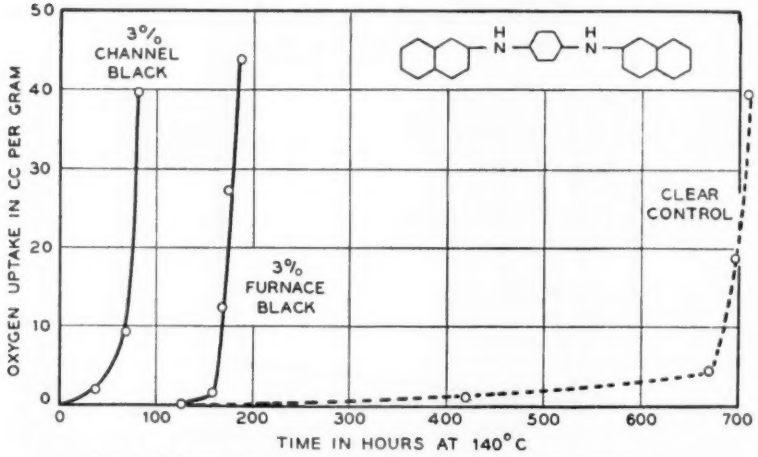

FIG. 6.—Influence of various carbon blacks on the antioxidant behavior of 0.1% *N,N'*-Di-β-naphthyl-*p*-phenylenediamine in polyethylene.

antioxidant, when present in only 0.1% concentration extends the initiation of oxidation from less than an hour for uninhibited polyethylene to approximately 500 hours at 140° C (Figure 4). Under these same conditions, 3% carbon black affords about 40 hours of protection. However, when both the antioxidant and carbon black are added to polyethylene, the effectiveness of the antioxidant is considerably reduced and protection against oxidation is less than 150 hours. This adverse effect has been observed generally with conventional amine or phenol antioxidants. The effect of two carbon blacks of comparable particle size, one an acidic carbon black of pH 4.5 and the other a basic furnace black of pH 7.5, on diphenyl-*p*-phenylenediamine is shown in Figure 5. The acidic carbon has a greater adverse effect than the basic carbon, but both reduce the effectiveness of this amine antioxidant. These data indicate that the adverse

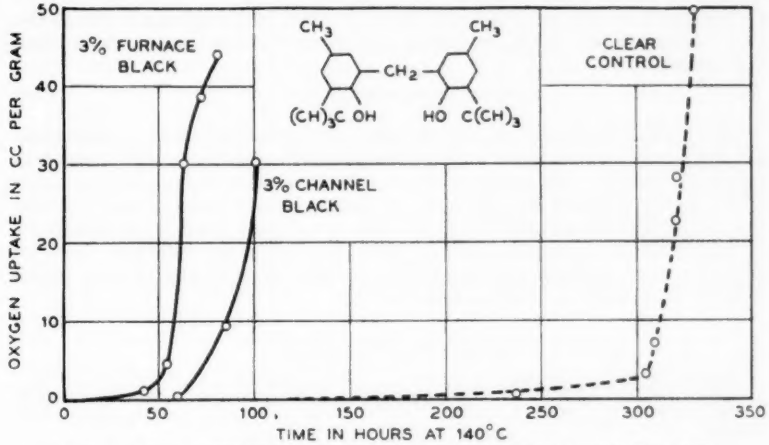

FIG. 7.—Loss of antioxidant effectiveness of 0.1% 2,2′-methylenebis-(4-methyl-6-*tert*-butyl phenol) in the presence of various carbon blacks.

effect may be due to adsorption and/or decomposition of the antioxidant by carbon black, the amine being more strongly adsorbed by the acidic carbon. Di-β-naphthyl-*p*-phenylenediamine is a somewhat better antioxidant for clear polyethylene than diphenyl-*p*-phenylenediamine. This antioxidant (Figure 6) is also affected to a greater extent by the acidic carbon. Both carbon blacks have a greater adverse effect on the larger dinaphthyl compound.

Phenol antioxidants have received considerable attention recently because they do not stain polyethylene as do the amines. Although most phenols are not good antioxidants for polyethylene, complex compounds such as 2,2′-methylenebis-(4-methyl-6-*tert*-butyl phenol) do give good protection to the clear polymer (Figure 7). In the presence of carbon black, however, this antioxidant loses almost all of its effectiveness. There is very little difference between the effect of the acidic and the basic carbon blacks although adsorption by the basic carbon appears to be slightly greater.

CONCLUSIONS

Carbon black has been shown to function as a mild thermal antioxidant for polyethylene at 140° C. The amount of protection increases with concentra-

tion and is dependent on the chemical nature of the carbon surface. This antioxidant effect is shown by a variety of carbon blacks with a considerable range of particle size, but very coarse carbons in comparable weight concentration exhibit no antioxidant effect. Recent studies concerned with the chemical nature of the carbon black surface indicate the presence of various oxygenated groupings which may account for the weak antioxidant activity of some carbon blacks.

In all cases examined, conventional amine and phenol antioxidants in polyethylene are adversely affected by carbon black. This effect can be attributed to adsorption followed by chemical decomposition of the antioxidant on the carbon black[5,6]. The chemical nature of the carbon black apparently influences the adsorption since the loss in activity of amine antioxidants is much more pronounced with acidic than basic carbon blacks. Whereas the effect of carbon black on antioxidant behavior is observed over a wide pH range, the effect decreases and finally disappears as the particle size of the carbon black is increased.

SYNOPSIS

About 3% by weight of carbon black adequately protects polyethylene against photo-oxidation and, under accelerated test conditions, slightly inhibits thermal oxidation. As a rule small amounts of organic antioxidants are also added to the polymer for optimum protection. Now many of the common phenolic and amine additives have been found to function much less effectively in polyethylene containing carbon black than in clear polymer. Loss of effectiveness is attributed to adsorption and/or decomposition of the antioxidant by both basic and acidic carbon black.

ACKNOWLEDGMENTS

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NEW THERMAL ANTIOXIDANTS FOR POLYETHYLENE CONTAINING CARBON BLACK *

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Carbon black in 2 or 3% concentration, which is often added to protect polyethylene against photo-oxidation, has an adverse effect on conventional antioxidants such as substituted phenols or secondary aromatic amines[1]. The protection which these antioxidants impart to clear polyethylene is considerably reduced when carbon black is added to the polymer. In contrast, certain organo-sulfur compounds have now been shown to be outstanding antioxidants in carbon-containing polymers, losing none of their effectiveness, but rather exhibiting a synergistic effect with carbon black. Furthermore, several organo-sulfur compounds which show no appreciable antioxidant activity in the clear polymer become excellent antioxidants in the presence of carbon black.

The relative effectiveness of the various antioxidants has been determined by direct measurement of the rate of oxygen absorption at 104° C. Similar measurements over a temperature range are now in progress and will be reported at a later date.

EXPERIMENTAL METHODS

The procedure for preparing samples and for measuring their oxidation rates was identical with that described in the preceding paper. Antioxidants were obtained from commerical sources or, when not available, were synthesized by conventional methods. In all instances where the melting point of the antioxidant under study was above 124° C, a master batch of antioxidant in polyethylene was first prepared. The master batch was then cut back to the desired antioxidant concentration. Carbon containing formulations were prepared from a 25% master batch of a typical channel black having a particle size of 180 A and pH of 4 to 5.

RESULTS AND DISCUSSION

Phenolic antioxidants, which have received considerable attention recently due to their non-staining characteristics, are usually less effective inhibitors for polyethylene oxidation than are the amines. Indeed, many of the common phenols in 0.1% concentration are no more effective than carbon black alone in 3% concentration. Even those which show moderate protection against oxidation lose most of their effectiveness in the presence of carbon black. Addition of long alkyl chains to the aromatic nuclei of many phenols improves their antioxidant activity[2], presumably through increased compatibility, but these modified phenols are no better in the presence of carbon black than the simple phenols from which they are derived.

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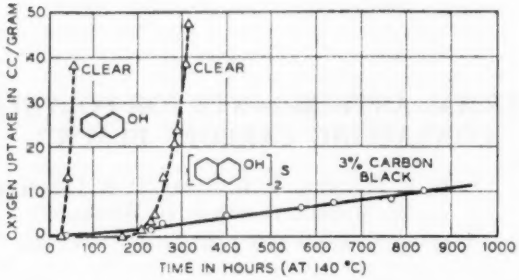


FIG. 1.—Relative effect of 2-naphthol and thiobis-(2-naphthol) in 0.1% concentrations on the thermal oxidation rate of polyethylene.

2-Naphthol (0.1%), which has been used extensively as a stabilizer in simple hydrocarbon systems, inhibits oxidation of polyethylene to about the same extent as 3% carbon black. However, when 2-naphthol is condensed with sulfur dichloride, the resulting thioether is not only more effective in the clear polymer, but is also a much better antioxidant in the presence of carbon black (Figure 1). In fact, the mixture of carbon black and thiobis-(2-naphthol) appears to be synergistic. The linear rate curve, showing no evidence of autocatalysis throughout the reaction, resembles that obtained with retarders rather than antioxidants[3]. Absence of autocatalysis may indicate that this carbon black-antioxidant combination prevents radical formation from reaction products like hydroperoxides. Either hydroperoxides are not formed in the presence of the sulfur compounds or, if formed, they do not decompose by a radical mechanism.

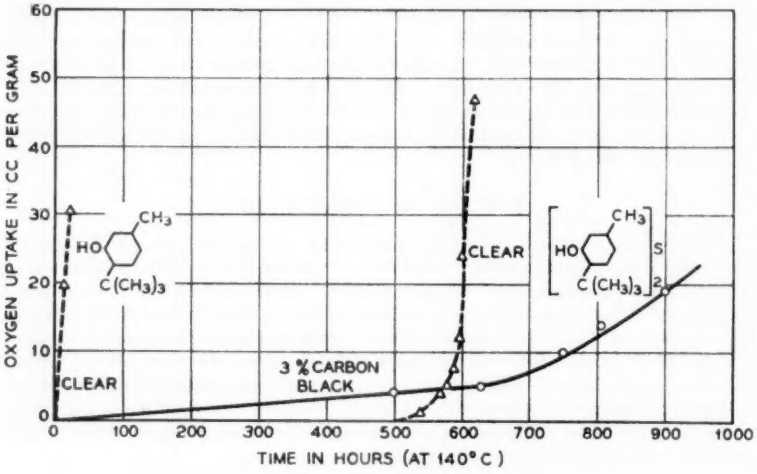
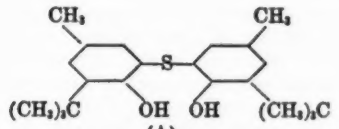


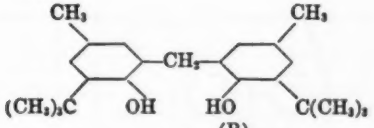
FIG. 2.—Thermal oxidation rate of polyethylene containing 0.1% 4,4'-thiobis-(3-methyl-6-*tert*-butyl phenol) in polyethylene.

The unusual effect of carbon black on thiobis-(2-naphthol) has been observed with many thioethers derived from moderate or weak antioxidants. For example, 3-methyl-6-*tert*-butylphenol is a poor antioxidant for polyethylene but its corresponding thioether, 4,4′-thiobis-(3-methyl-6-*tert*-butylphenol), is a very good antioxidant in clear polyethylene and exhibits a synergistic effect with carbon black (Figure 2). In this instance the rate curve in the presence of carbon black shows some evidence of autocatalysis, but the steady state rate is much lower than that observed with this compound in clear polyethylene. 5-Pentadecyl-1,3-benzenediol, in contrast, is a good antioxidant in clear polyethylene and little improvement results from condensation to a thioether. The condensation product does, however, show the synergism typical of thioethers when carbon black is present. Similarly N-phenyl-2-naphthylamine, a good amine antioxidant for polyethylene, is not substantially improved by conversion to a thioether except in the presence of carbon black. Phenothiazine, however, is only about half as effective in the presence of carbon black as in the clear polymer. In this instance, where the sulfur atom is part of the ring system, the compound does not show the synergism with carbon black characteristic of the substituted thioethers.

Results obtained with two commercial antioxidants having the following chemical structures indicate that the effect of carbon black can be attributed to the thioether bond.



(A)
2,2′-Thiobis-(4-methyl-6-*tert*-butylphenol)



(B)
2,2′-Methylenebis-(4-methyl-6-*tert*-butylphenol)

These compounds differ only in the nature of the bridge between the aromatic rings. Whereas the methylenebis compound (B) loses most of its antioxidant activity when carbon black is present (Figure 3), the degree of protection derived from the combination of carbon black with the corresponding thioether (A) is greater than would be anticipated from the activity of each component. Thus a variety of relatively inferior inhibitors may be modified by coupling with sulfur dichloride. Antioxidant activity is thereby increased in clear polyethylene to varying degrees and generally is further improved in the presence of carbon black. The improvement is not due to greater retention of the sulfur compound resulting from a gain in molecular weight, because many of the thioethers have vapor pressures as high as some of the less effective antioxidants. The presence of active hydrogen in hydroxyl or amine groups is essential, however, since on methylation these substituted thioethers are no

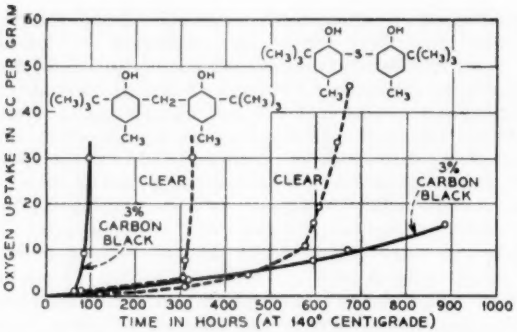


FIG. 3.—Comparison of 0.1% 2,2'-thiobis-(4-methyl-6-*tert*-butyl phenol) with 0.1% 2,2'-methylenebis-(4-methyl-*tert*-butyl phenol) as an antioxidant for polyethylene.

longer effective as antioxidants either in clear or carbon black formulations. In this respect the thioethers resemble conventional antioxidants. However, the difference in behavior in the presence of carbon black between thioethers which contain active hydrogen and conventional antioxidants seems enough to indicate that two different mechanisms are involved.

Perhaps the most direct evidence supporting this suggestion has been found in the remarkable antioxidant properties of compositions containing carbon black and sulfur compounds lacking amino and phenolic groups and having no other active hydrogens. Such compounds would not be expected to function as conventional antioxidants, and consequently any protective action must result from reactions involving the sulfur bond. For example, benzylthiobenzene, though it does not inhibit the oxidation of clear polyethylene, becomes

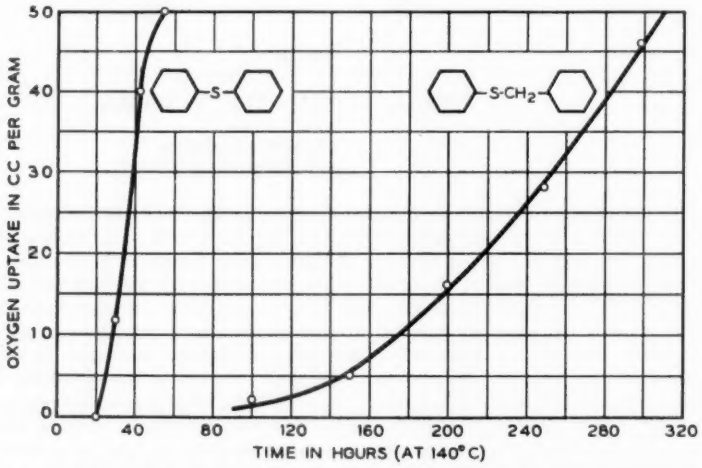


FIG. 4.—Relative effectiveness of phenyl sulfide and phenyl benzyl sulfide in 0.1% concentrations on the thermal oxidation rate of polyethylene containing 3% carbon black.

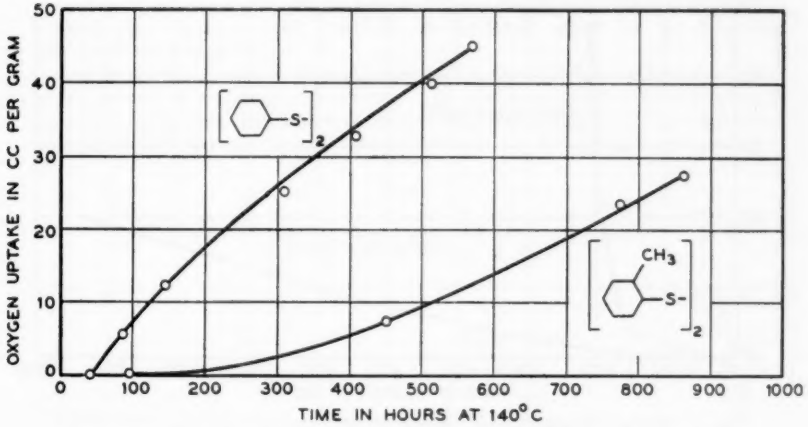


FIG. 5.—Relative effectiveness of phenyl disulfide and 2-tolyl disulfide in combination with 3% carbon black as thermal antioxidants for polyethylene.

a good antioxidant in the presence of carbon black (Figure 4). Benzyl sulfide and 2-(2-propenylthio)-naphthalene are also effective, but only in combination with carbon black. Each of these thioethers has a relatively weak bond between sulfur and the carbon of a methylene group. In contrast, phenylsulfide, with a much stronger carbon-sulfur bond, does not have antioxidant activity either in clear polyethylene or in the presence of carbon black.

The behavior of phenyl disulfide in polyethylene containing carbon black, as shown in Figure 5, is further evidence for a relationship between bond strength and antioxidant activity. In this instance the weaker bond would presumably be between the two sulfur atoms. Disulfides in general give good protection against polyethylene oxidation but only in carbon black compositions. Alkylation of the aromatic nuclei, exemplified by 2-tolyl disulfide in Figure 5, increases antioxidant efficiency. Similarly 2-naphthyl disulfide is much more effective than phenyl disulfide. Heterocyclic disulfides, such as 2-benzothiazolyl disulfide, are also effective antioxidants with carbon black.

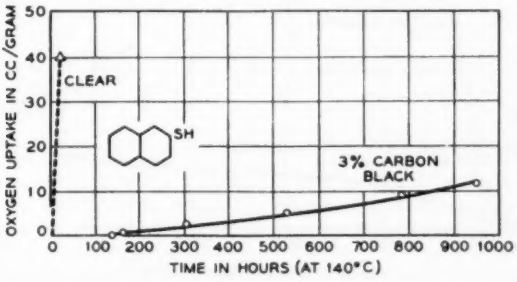


FIG. 6.—2-Naphthalenethiol in 0.1% concentration as an antioxidant for polyethylene in the presence of 3% carbon black.

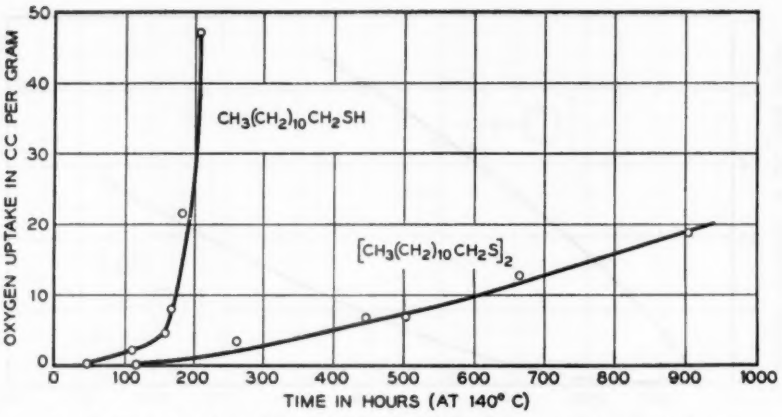


FIG. 7.—Effect of 1-dodecanethiol and 1-dodecyl disulfide in 0.1% concentrations on the thermal oxidation rate of polyethylene containing 3% carbon black.

These data indicate a relationship between bond strength and the ability of these compounds to function as antioxidants in the presence of carbon black.

Results obtained with disulfides containing no active hydrogen indicate that the corresponding thiols should also be considered as potential antioxidants. 2-Naphthalenethiol provides very little protection for clear polyethylene but becomes an excellent antioxidant in the presence of carbon black. This thiol-carbon black composition, as shown in Figure 6, exhibits a gradual, linear oxygen uptake over a period of 2000 hours without reaching an accelerating stage. The degree of protection imparted to polyethylene under accelerated

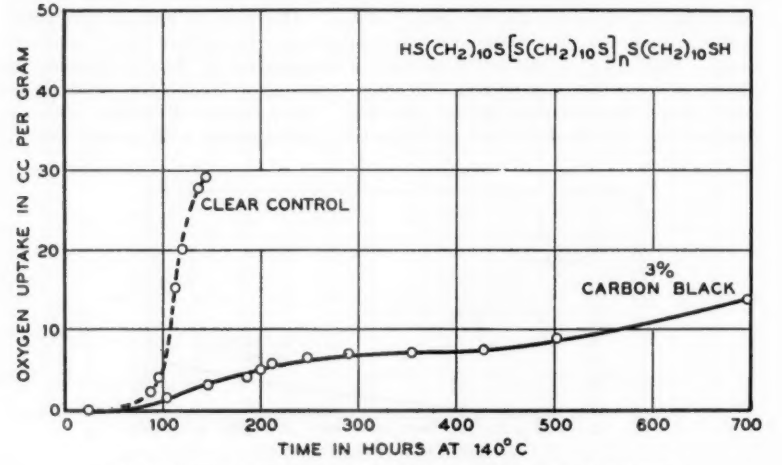


FIG. 8.—Thermal oxidation rate of polyethylene containing 0.1% of a polymer derived from 1,10-decamethylenedithiol.

test conditions by the combination of carbon black and 2-naphthalenethiol exceeds that obtained with previous antioxidants except for the thioether derived from 2-naphthol.

At lower temperature, 2-naphthalenethiol does inhibit oxidation of clear polyethylene to a very slight extent. The low level of activity, however, is much less than that observed with 2-naphthol. This may be interpreted as an indication that the active hydrogen in thiols is not primarily a terminator of

TABLE I

SUMMARY OF THE EFFECT OF ORGANO-SULFUR COMPOUNDS IN 0.1% CONCENTRATION ON THE OXIDATION OF POLYETHYLENE WITH AND WITHOUT CARBON BLACK

Compound	Reference to method of synthesis	M.p., °C	Hours to absorb 10 cc O_2/g	
			Clear	3% carbon black
Polyethylene controls	Commercial		6	35
Elemental sulfur (1%)	Commercial		—	120
Thioethers				
4,4′-Thiobis-(3-methyl-6-*tert*-butylphenol)	5	160	600	750
Thiobis-(2-naphthol)	5	214	240	730
Thiobis-(*N*-phenyl-2-naphthylamine)	5	184	190	260
Benzylthiobenzene	7	41–42	6	180
Methylthio-2-naphthalene	8	64–65	6	55
2-Naphthyl thiobenzoate	6	107	6	70
4-Aminophenyl sulfide	10	110–111	15	35
Disulfides				
Phenyl disulfide	Commercial		6	120
2-Tolyl disulfide	Commercial		6	520
2-Acetamidophenyl disulfide	12	155–156	6	480
1-Dodecyl disulfide	9	34	20	520
2-Benzylthiazolyl disulfide	Commercial		8	350
4,4′-Dithiodimorpholine	Commercial		120	600
Polymeric 1,10-decanedithiol	9	64–65	110	540
Thiols				
2-Toluenethiol	Commercial		6	200
2-Naphthalenethiol	Commercial		6	900
2-Mercaptobenzothiazole	Commercial		35	380
1-Dodecanethiol	Commercial		6	160
1,10-Decanedithiol	Commercial		16	200
Miscellaneous				
Thianthrene	Commercial		20	230
Phenothiazine	Commercial		430	250
2-Naphthyl diselenide	11	129–130	19	200

the oxidative chain, or, as suggested by Hammond and coworkers[4], that hydrogen abstraction is not the rate-controlling step in antioxidant reactions. Wide variations have been noted in antioxidant behavior of other thiol-carbon black compositions. The toluene thiols, for example, present an interesting trend from the para isomer which follows the ordinary rate curve for conventional antioxidants to the ortho isomer which behaves more like a retarder.

Nearly all commercial organic antioxidants contain aromatic groupings such as those in the thioether, thiol, and disulfide compounds discussed thus far.

Few aliphatic substances have approached the activities attained with even mediocre aromatic antioxidants. However, in conjunction with carbon black, alkyl disulfides, such as 1-dodecyl disulfide, or thiols, such as 1-dodecanethiol and 1,10-decanedithiol (Figure 7), and also polymers of alkyl dithiols (Figure 8) have been found to be good antioxidants for polyethylene. Polymeric antioxidants have the added advantage of providing variations in concentrations of active sulfur groupings over a wide range of molecular weight, allowing better retention of the sulfur compound by the polymer substrate. The various groups of sulfur antioxidants are summarized in Table I with typical examples of each group and references to the synthetic method used.

Certain thiols and disulfides provide slight protection for clear polyethylene. The active hydrogens in thiols might function to some extent as chain terminators since methylation of 2-naphthalenethiol to methylthionaphthalene nullifies the antioxidant effectiveness both in the clear polymer and in the presence of carbon black. However, another mechanism is required to adequately explain the behavior of disulfides. Inhibition by disulfides in clear polymer resembles reactions proposed for compounds such as 10,10′-diphenothiazine[13], tetraphenylhydrazine[14], and tetramethyl-1,4-benzenediamine[15]. Furthermore, the thermal initiation of styrene polymerization by certain disulfides[16] indicates the formation of radicals by sulfur-sulfur bond cleavage. Carbon black may tend to promote rupture of —S—X bonds where X is S, H, $-CH_2AR$, $-\overset{\overset{O}{\|}}{C}Ar$, etc. The resulting product, RS·, in a free state or combined with carbon black may then trap radical intermediates in polymer oxidation. Conversely, the sulfur compounds may merely prolong and accentuate the antioxidant properties of the carbon surface. In that event the sulfur compound would not function as an antioxidant at all, but would promote or possibly regenerate the inhibiting effect of the carbon.

CONCLUSION

Antioxidants which contain a thioether bond are usually more effective than the simple compounds from which they are derived. More significant is the effect of carbon black on these improved antioxidants, generally resulting in even greater protection than in the clear polymer. This is in contrast to the behavior of conventional antioxidants which do not contain a thio-bond. In all cases examined, these conventional antioxidants lose a large proportion of their effectiveness in the presence of carbon black. Recent studies concerned with the chemical nature of the carbon black surface strongly suggest the presence of reactive chemical groupings which may account for the weak antioxidant activity of some carbon blacks. Apparently the carbon black surface interacts with organo-sulfur antioxidants since this unique behavior has not been observed in other materials of comparable particle size, such as alumina, titania, or silica, nor do these materials themselves inhibit polyethylene oxidation.

Thioethers and disulfides which contain no amine or phenol groups and hence no active hydrogen constitute another class of antioxidants which are unusual in that they attain a significant degree of activity only in the presence of carbon black. Although the mechanism through which these simple compounds function as antioxidants has not been established, there is considerable evidence that a relationship exists between antioxidant activity and bond dissociation energy. Some thiols may act to a slight extent as conventional antioxidants

in clear polyethylene, but when carbon black is present, they appear to function through the same mechanism as do the simple organo-sulfur compounds which contain no active hydrogen. It is significant that within the general class of organo-sulfur antioxidants, alkyl compounds exhibit strong antioxidant activity in the presence of carbon black, and are often comparable with their aromatic counterparts.

SYNOPSIS

Common secondary aromatic amine and alkylated phenolic antioxidants lose much of their activity in polyethylene containing carbon black. In contrast their thioether derivatives provide more protection against oxidation than the sum of the separate contributions of carbon black and the sulfur compounds. Organic disulfides and some thio-ethers without amino or phenolic hydrogen also safeguard polyethylene from oxidation but only in the presence of carbon black. Likewise thiols are excellent protectants in combination with carbon black but not in clear polymer. Aliphatic thiols, disulfides, and their polymeric derivatives and related selenium compounds exhibit similar activity.

ACKNOWLEDGMENT

The authors wish to thank Dr. B. S. Biggs for stimulating discussions during the course of these studies.

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CARBON BLACK STRUCTURE AND THE TEAR RESISTANCE OF VULCANIZATES *

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INTRODUCTION

Tear resistance is one of the most important properties of vulcanized rubber. The procedure for testing samples by tearing them apart amounts to the growth of a crack. The practical significance of appraising tear strength is very great, since in actual service, the failure of a manufactured article could be brought about by the growth or propagation of any crack which might be present. But the study of tear resistance is also of theoretical interest. The process of failure consists of two stages: initiation of tearing and propagation of the initial tear. Tear strength (resistance to the growth of a cut) characterizes the capacity of the vulcanized rubber for inhibiting the evolution of this second stage of the tearing process.

It has been pointed out in a number of investigations that an improvement in tear strength can be achieved by loading the rubber compounds with active fillers[1]. A relation was shown between the activity of the fillers, the characteristices of the surface of the cracks and the degree of tear resistance[2,3].

Dogadkin advanced the hypothesis that active carbon blacks enhance tear resistance because of a deterrent effect on crack growth of the short carbon black chains[4].

The references cited shed light on the problem of the effect of the properties of different blacks on tear resistance at various test temperatures.

EXPERIMENTAL

Tear resistance was determined in accordance with GOST 20–41. The tests were made with dynamometers, in chambers with controlled temperatures of 20, 40, 70, 100 and 120° C.

The test specimens were from vulcanizates of the following rubbers: masticated natural (NR), butadiene-styrene (SKS-30)—with a Karrer plasticity of 0.50—and sodium-butadiene rubbers (50 Mooney). They were loaded with various carbon blacks (channel, anthracene, acetylene, gas, furnace, oil-furnace and thermal), in proportions of 20, 40, 60, 80, and 100 parts by weight per 100 parts by weight of rubber.

The recipes for the vulcanized compounds were as follows (in parts by weight):

1. NR: 100; sulfur: 2; mercaptobenzothiazole (MBT): 0.6; stearic acid: 2.0; zinc oxide: 5.0; Rubrax: 5.0; carbon blacks: in varying proportions.
2. SKB: 100; sulfur: 1.5; MBT: 1.8; zinc oxide: 5.0; Rubrax: 5.0; blacks: in varying proportions.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by G. Leuca from *Kauchuk i Rezina* **18**, No. 1, pages 27–30 (1959).

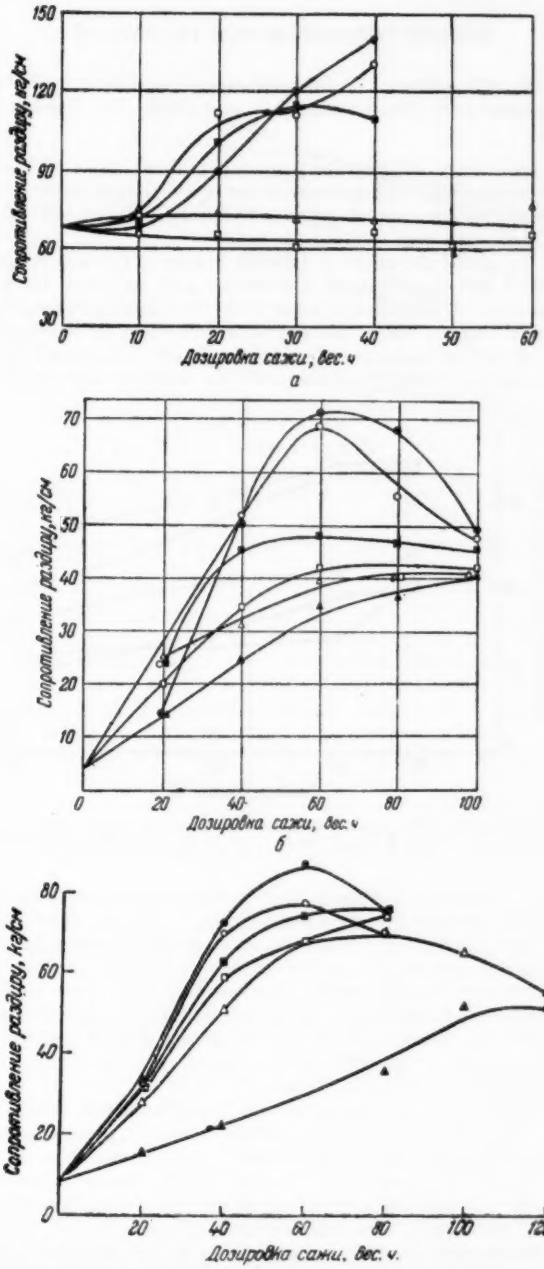

FIG. 1.—The tear resistance of vulcanizates as a function of the proportion of different carbon blacks: upper graph (a) natural rubber vulcanizates; middle graph (b) SKB vulcanizates; lower graph (c) SKS-30 vulcanizates. ● channel blacks; △ furnace blacks; ○ anthracene blacks; □ oil-furnace blacks; ■ acetylene blacks; ▲ thermal blacks. Ordinate: tear strength in kg/cm; abscissa: carbon black proportions, parts by weight.

3. SKS-30: 100; sulfur: 1.7; dibenzothiazolyldisulfide: 1.0; diphenylguanidine: 0.5; stearic acid: 2.0; Rubrax: 5.0; zinc oxide: 5.0; blacks: in varying proportions.

Mixing took place on laboratory mixing mills at 40° C. There was an extension of mixing time with increase in the proportion of blacks. Vulcanization of the samples was carried out in a hydraulic press at 143° C. Samples having optimum cure were used for the tests.

Figure 1 (a) shows the effect of different blacks on the tear strength of NR vulcanizates at 20° C. Channel, anthracene and acetylene blacks improve the tear resistance of vulcanizates made from crystallizing natural rubber, but furnace and oil furnace blacks did not show any effect on this property. At small doses, all carbon blacks proved to be the same in enhancing tear resistance. With vulcanizates of noncrystallizing rubbers (SKS-30 and SKB) all blacks

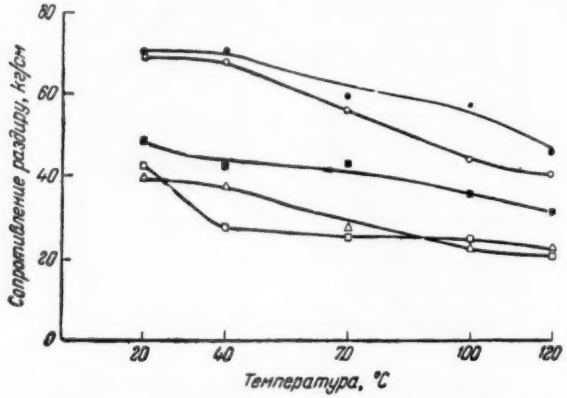

FIG. 2.—Tear strength of SKB vulcanizates, loaded with 60 parts by weight of different carbon blacks, as a function of the temperature. ● channel black; ○ anthracene black; ■ acetylene black; △ furnace black; □ oil-furnace black. Abscissa: temperature; ordinate: tear strength, kg/cm.

improved tear resistance but there were certain differences between the two groups of blacks though they were less distinct, to be sure, than those for vulcanizates of natural rubber. When the carbon black content is 20 parts by weight the tear resistances of synthetic rubber vulcanizates loaded with different blacks are approximately equal. Increased loadings, from 40–60 parts by weight of channel and anthracene blacks, will result in considerably greater tear resistance than the use of furnace and oil furnace blacks. With further increase in the loading to 80–100 parts by weight, the differences between the various blacks become negligible, Figures 1(a) and 1(c).

Figure 2 shows the dependence of tear strength on test temperatures, for vulcanized rubber from SKB containing different blacks, proportion 60 parts by weight. In vulcanizates filled with channel or anthracene blacks, raising the temperature to 40° has practically no effect on the degree of tear resistance. At the highest temperatures used the resistance to tearing was somewhat reduced. For vulcanizates containing furnace, oil furnace and thermal blacks any rise in temperature leads to a considerably greater diminution in the tear strength as compared to vulcanizates loaded with the same amounts of channel

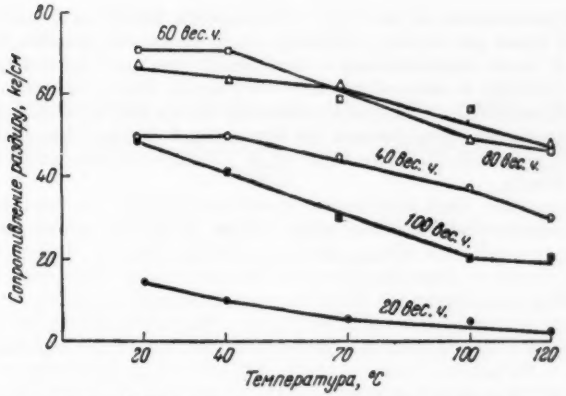

FIG. 3.—Tear strength of SKB vulcanizates containing varying proportions of channel blacks as a function of the temperature, at 20, 40, 60, 80 and 100 parts by weight. Abscissa: temperature; ordinate: tear strength, kg/cm.

or anthracene blacks. This phenomenon was also noted by Pechkovskoi and Dogadkin[5].

A dependence of the tear strength on the temperature is indicated, Figure 3, when higher proportions of channel black are used. For vulcanizates with 20 and 100 parts by weight of carbon blacks elevated temperatures cause considerable reductions in tear strength. When the carbon black loading is 40, 60 and 80 parts by weight this property is less dependent on the rise in temperatures.

Table I presents the temperature stability coefficients of vulcanized SKB and SKS-30, containing blacks in different proportions. Heavy loading with furnace, oil furnace and thermal blacks leads to an increase in the coefficients; with acetylene, channel and anthracene blacks the value of the temperature coefficient as a function of loading goes through a maximum (in addition, for acetylene black, the maximum is found at lesser loadings than is the case with channel or anthracene blacks).

DISCUSSION OF RESULTS

Our results substantiate the theory that an increase in tear resistance, through the introduction of carbon black into the compounded vulcanizate, is

TABLE I

HEAT STABILITY COEFFICIENTS* FOR TEAR RESISTANCE OF SKB AND SKS-30 VULCANIZATES, LOADED WITH DIFFERENT PROPORTIONS OF BLACKS

	Rubber							
	SKB				SKS-30			
	Black, phr							
Carbon black	20	40	60	80	20	40	60	80
Channel	30	56	79	62	30	49	62	60
Anthracene	30	58	56	53	28	57	64	49
Acetylene	—	62	55	56	55	53	69	50
Oil furnace	31	39	45	44	32	29	39	38
Thermal	—	23	31	48	43	48	—	43
Furnace	18	25	53	64	22	26	32	41

* % retention of tear strength at high temperature.

related to the structure of the black. As is known, blacks are divided into two groups: 1) those not forming secondary chain structures (nonstructure-forming) and 2) those demonstrating a considerable tendency toward bonding of the black particles to each other and a readiness to form continuous chainlets from black particles, joined to one another in such a way as to give rise to secondary structures[6]. The furnace, oil furnace and thermal blacks belong to the first type of blacks. The other type includes channel, anthracene and acetylene blacks.

The secondary black structure evidently guarantees a notable increase in the tear resistance of the vulcanizates. Thus, in natural rubber vulcanizates displaying strength even without the introduction of blacks, the tear resistance is improved only by those blacks which form secondary structures. For synthetic rubber vulcanizates all blacks increase this stability, so that an improvement in tear resistance is noted in each case. But the incorporation of channel and anthracene blacks induces a greater increase in the tear resistance. The difference in the action of various blacks is noted only in those cases where they are employed in amounts necessary for the production of continuous secondary black structures. At low loadings (20 parts by weight) significant differences were not observed between structure-forming and nonstructuring blacks.

The formation of secondary black structures leads to the appearance of short chains of black particles. In conformance with the hypotheses of Dogadkin[4] these chainlets, with elongation of the vulcanized rubber, are capable of orientation perpendicular to the direction taken by the tear propagation. Owing to the greater stability of these formations of the black particles and the greater strength of the bonds between the particles, the tear, when it reaches each chainlet, changes the direction of its growth and thus the resistance to tearing is enhanced.

Secondary black structures impart a definite thermal stability. Consequently, when blacks promoting such structures are introduced, in the loadings required for chain formation, an increase in the temperature will not occasion such a diminution of the tear resistance, as takes place in vulcanized rubbers containing gas, furnace or thermal blacks, or channel, anthracene and acetylene blacks in small concentrations.

It can be assumed that when blacks are added, which induce the building of secondary structures, an increase in temperature has almost no effect on the tear strength of vulcanizates.

CONCLUSIONS

1. The increase in tear resistance of vulcanizates, where carbon blacks are added in considerable amounts, is related to the formation of secondary black structures and is manifested especially when certain blacks are used (channel, anthracene and acetylene).

2. The presence of secondary black structures brings about an increase in the tear resistance at elevated temperatures.

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EFFECTS OF THE TYPES OF RUBBER AND CARBON BLACK ON THE FORMATION OF CARBON-RUBBER GEL *

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Addition of carbon black to rubber mixtures results in increased modulus and higher tensile, tearing and abrasion strength. This effect is evidently determined to a considerable extent by the bonds formed between the rubber and carbon in the mixture.

In a number of recent investigations the bonding between rubber and carbon black has been studied by determinations of the socalled carbon-rubber gel, which is the portion of the nonvulcanized rubber mix insoluble in benzene. According to Dogadkin and Feldshtein[5] the proportion of the insoluble fraction depends on the activity of the filler. It has also been shown that the amount of carbon-rubber gel depends on the molecular weight of the rubber[1,2], the type of carbon black (mainly its degree of dispersion)[2,4], and on the compounding temperature[3,6].

It is believed that the formation of a carbon-rubber gel is the result of formation of a carbon network (as was proved by Dogadkin[7]), of the considerable energy of intermolecular interaction between the rubber and the carbon, and of the entanglement of the flexible molecular chains of the rubber[1].

The formation of a carbon-rubber gel has been associated with rubber reinforcement in a number of papers[1,2,6,8]. It has been shown that an increase in the amount of carbon-rubber gel corresponds to an increase in the modulus and the abrasion resistance of vulcanizates[6,7].

Carbon-rubber gel determinations are not particularly accurate, but they may be used for estimating bond strengths in rubber-carbon black mixtures. For determining the nature of these bonds, we studied the formation of carbon-rubber gels in mixtures of natural and synthetic rubber with various carbon blacks, and estimated gel stability under various extraction conditions.

EXPERIMENTAL

The following rubbers were taken for the investigation: natural rubber (NR) (smoked sheet), SKB 50, SKBM 50, thermally plasticized SKS-10 and SKS-30 A with plasticity 0.5, and the following carbon blacks: channel, acetylene, nozzle furnace, and thermal.

The molecular weights of the rubbers were calculated from viscometric data by the formulas:

For NR $[\eta] = 5.02 \cdot 10^{-4} \cdot M^{0.67}$

For SKS $[\eta] = 4.4 \cdot 10^{-4} \cdot M^{0.67}$ Ref. 11.

For SKB and SKBM $[\eta] = 2.7 \cdot 10^{-4} \cdot 10\ M^{0.725}$ Ref. 12.

* Reprinted from *Colloid Journal* 19, 645–650 (1958); a translation by Consultants Bureau, Inc. of *Kolloid. Zhur.* 19, 644–650 (1958).

the values being 126,000 for NR, 85,500 for SKB, 106,200 for SKBM, 172,600 for SKS-10, and 102,000 for SKS-30A.

The characteristics of the carbon blacks are given in Table I.

The mixtures were milled on laboratory mills, with roll diameter 160 mm, at 20–30°, in the following formulation:

Rubber	100	parts by weight
Stearic acid	3.0	parts by weight
Rubrax	5.0	parts by weight
Carbon	from 10 to 180	parts by weight

The compounding time increased with the carbon black content, and ranged from 10 to 20 minutes.

The compounded mixtures were left for 24 hours, and the rubber-carbon gel contents were then determined as follows: a weighed sample of 2.0 g of the finely shredded mixture was placed in a weighed textile cartridge. The cartridge was placed in a wide-necked Erlenmeyer flask and covered with benzene or carbon tetrachloride. The extraction was continued for 24 and 48 hours at 20°, and for 18 hours in boiling benzene at 78°. At the end of the extraction

TABLE I

CHARACTERISTICS OF THE CARBON BLACKS[10]

Type of carbon	Average particle diameter, A	pH	Oil adsorption, ml/g
Channel	280	3.5–4.5	1.4
Acetylene	400	6.5–7.0	2.8
Furnace	640	9–10	0.8
Nozzle	1100	9–10	3.0
Thermal	1880	7–8	0.3

the solvent was decanted, the cartridge was washed once with ligroine, and dried in a thermostat at 60° to constant weight. The carbon-rubber gel content was determined as the ratio of the weight of the dry gel to the weight of the sample. The reproducibility of the results was within 2–3%. The carbon content of the carbon-rubber gels was determined by the method used for determination of carbon black in vulcanizates (by decomposition of the gel in nitric acid sp. gr. 1.37). The fraction of the rubber bound with carbon was calculated from the results.

The results of the carbon-rubber gel determinations for NR, SKB and SKS-30A rubbers are shown in Figure 1. The following comments may be made on the results.

The carbon-rubber gel content increases with the amount of carbon black added. For example, thermal black, which does not form a gel when added in small amounts, forms a large amount of gel when added in 150–180 parts by weight. The carbon-rubber gel content for a definite amount of carbon depends on the type of carbon black added. At contents of 20–40 parts by weight, the carbons form the following sequence: acetylene, channel, nozzle, furnace, thermal. The carbon-rubber gel content depends on the type of rubber. In synthetic rubbers (SKB, SKS-30A) gel formation occurs to a greater extent and with smaller additions of carbon black than in natural rubber, despite the somewhat lower molecular weight of these rubbers.

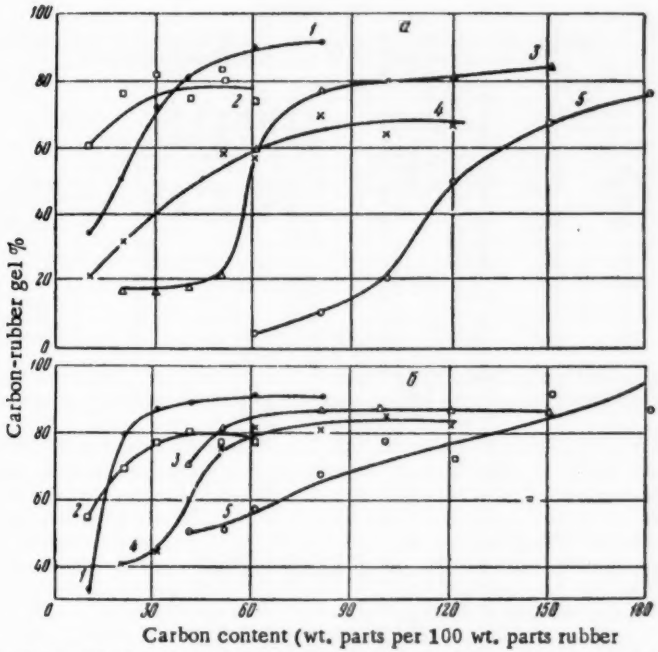

FIG. 1.—Contents of carbon-rubber gel in mixtures based on NR (a) and SKS-30A (b) with different carbon contents: *1*) channel black; *2*) acetylene black; *3*) furnace black; *4*) nozzle black; *5*) thermal black.

The variations of the carbon-rubber gel content with extraction conditions are given in Tables II and III.

It follows from Tables II and III that the more harsh conditions of benzene extraction (boiling, or increase of extraction time) do not cause decomposition of the carbon-rubber gel, but only decrease its content somewhat; this effect is more prominent in mixtures with small amounts of carbon black.

The amounts of gel formed when the mixtures are dissolved in carbon tetrachloride are somewhat greater than when they are dissolved in benzene for

TABLE II

VARIATIONS OF CARBON–RUBBER GEL CONTENTS IN MIXTURES BASED ON NR WITH THE EXTRACTION CONDITIONS

Type of carbon black	Wt parts of carbon to 100 wt parts rubber	Carbon—rubber gel, content, %			
		Benzene			CCl_4
		24 hrs 20°	48 hrs 20°	18 hrs 78°	48 hrs 20°
Channel	30	83.0	74.0	68.0	80.0
	80	92.0	83.0	82.0	—
Acetylene	20	77.0	67.0	63.0	79.0
	50	81.0	72.0	62.0	72.0
Furnace	80	79.0	78.0	72.0	84.0
Nozzle	80	70.0	61.0	60.0	75.0
Thermal	180	77.0	73.0	72.0	73.0

TABLE III

VARIATIONS OF CARBON-RUBBER GEL CONTENTS IN MIXTURES BASED ON SKB WITH THE EXTRACTION CONDITIONS

Wt. parts carbon to 100 wt parts rubber	Channel			Acetylene			Furnace			Nozzle			Thermal		
	Benzene		CCl_4	Benzene		CCl_4	Benzene		CCl_4	Benzene		CCl_4	Benzene		CCl_4
	24 hrs	48 hrs	48 hrs	24 hrs	48 hrs	48 hrs	24 hrs	48 hrs	48 hrs	24 hrs	48 hrs	48 hrs	24 hrs	48 hrs	48 hrs
10	69.0	42.0	—	82.0	59.0	58.0	—	44.0	—	43.0	43.0	—	—	—	—
20	86.0	75.0	83.5	89.0	65.0	71.0	57.0	56.0	—	64.0	43.0	—	—	—	—
30	81.0	74.0	—	—	—	—	65.5	52.0	—	87.0	66.0	60.5	—	40.8	—
40	86.0	70.0	83.5	—	—	—	76.0	62.0	—	—	—	78.0	58.0	46.0	—
50	—	88.0	—	—	—	—	87.0	64.0	68.0	80.0	77.0	76.0	62.0	54.0	—
60	86.0	86.0	82.0	85.0	66.0	78.0	87.0	66.0	—	90.0	76.0	79.0	83.0	60.0	—
80	—	—	—	—	—	—	89.0	75.0	74.0	—	—	—	83.0	68.0	58.0
100	—	—	—	—	—	—	82.0	73.0	74.0	—	—	—	—	69.0	62.0
120	—	—	—	—	—	—	—	—	—	—	—	—	82.0	69.0	71.0
180	—	—	—	—	—	—	—	—	—	—	—	—	86.0	73.0	73.0

TABLE IV

CONTENTS OF CARBON BLACK AND RUBBER BOUND WITH CARBON IN CARBON–RUBBER GELS IN MIXTURES BASED ON NR

Type of carbon black	Wt parts carbon to 100 wt parts rubber	Benzene, 48 hrs. 20°: Carbon content in gel, %	Benzene, 48 hrs. 20°: Amount of rubber bound with carbon, %	Benzene, 18 hrs. 78°: Carbon content in gel, %	Benzene, 18 hrs. 78°: Amount of rubber bound with carbon, %	CCl_4, 48 hrs. 20°: Carbon content in gel, %	CCl_4, 48 hrs. 20°: Amount of rubber bound with carbon, %
Channel	30	31.7	69.8	32.4	60.0	23.6	84
	80	68.5	48.0	57.6	64.0	48.8	—
Acetylene	20	47.0	45.4	32.5	44.3	27.0	52.0
	50	69.1	34.0	54.5	40.6	54.5	82.6
Furnace	80	77.6	33.0	62.0	48.3	63.4	72.2
Nozzle	80	84.0	18.5	75.5	26.2	56.0	51.6
Thermal	180	90.0	21.8	83.7	33.3	83.5	35.3

mixtures containing channel and acetylene blacks, approximately the same for mixtures with furnace and nozzle blacks, and less for mixtures with thermal black.

Table IV contains data on the contents of carbon black in the carbon-rubber gels for different extraction conditions and types of carbon. These results show that: 1) the content of carbon in the gel increases with increasing amount of carbon added to the mixture; 2) in mixtures containing furnace and nozzle blacks, with a lower gel content (see Table II) the carbon content of the gel is higher than in mixtures containing carbon black; 3) more harsh extraction conditions—the use of a more active solvent (CCl_4) or boiling—lead to a decrease of the carbon black content in the gel, i.e., carbon black is removed to a greater extent than rubber.

The contents of carbon-rubber gel in mixtures based on various rubbers before and after additional mastication are given in Table V. The mixture was masticated for 20 minutes on laboratory rolls at 20–30°. The gel contents are not appreciably affected by changes in the type of synthetic rubber (increased contents of butadiene residues in the 1,4 position or decreased contents of

TABLE V

EFFECTS OF MASTICATION ON THE CONTENTS OF CARBON–RUBBER GEL AND OF CARBON IN THE GEL (BENZENE EXTRACTION FOR 24 HOURS AT 20°)

Type of rubber	Type of carbon black	Wt parts carbon to 100 wt parts rubber	Contents of carbon-rubber gel, %: Before treatment	Contents of carbon-rubber gel, %: After 20 minutes of mastication	Contents of carbon in carbon-rubber gel, %: Before treatment	Contents of carbon in carbon-rubber gel, %: After 20 minutes of mastication
NK	Channel	60	92.0	83.0	43.6	46.0
	Furnace	100	86.0	86.0	53.0	57.3
SKB	Channel	60	89.0	90.0	40.0	40.7
	Furnace	100	90.0	88.0	60.0	53.5
SKBM	Channel	60	90.0	88.0	48.0	—
	Furnace	100	92.0	87.0	52.0	56.7
SKS-10	Channel	60	94.0	91.0	39.8	39.0
	Furnace	100	95.0	91.0	64.0	—
SKS-30A	Channel	60	95.0	91.0	—	40.9
	Furnace	100	86.0	85.0	56.3	61.0

styrene residues). In the case of a mixture of NR with channel black the amount of gel decreases after mastication; this is possibly caused by degradation of the rubber. This effect is slight for other types of rubbers.

DISCUSSION OF RESULTS

The view has been put forward in a number of papers[2,6] that formation of carbon-rubber gels can be largely attributed to the high stability of the bonds between the rubber molecules and the carbon black. It was considered that only active blacks form carbon-rubber gels[6]. It had also been suggested that chemical bonds may be formed between the rubber and the carbon black[9].

It is known that carbon blacks differ in their tendency to form carbon structures. Channel and acetylene blacks readily form continuous structures in rubber mixtures, consisting of chains of carbon particles. This property is not found in furnace and especially in thermal blacks[7]. According to our results, the ease of formation of a carbon-rubber gel depends on the tendency of the carbon black to form structures. In mixtures containing acetylene or channel blacks, appreciable amounts of gel are formed at lower carbon contents than in mixtures containing nozzle furnace, or thermal blacks. Acetylene black, which has a greater tendency to structure formation, forms large amounts of gel at lower contents than channel black, although the latter is highly disperse. The same applies to nozzle black. Though the particle size of nozzle black is greater than that of furnace black; the former forms appreciable amounts of gel at lower contents than does furnace black. On the other hand, on increase of the amount of semiactive or inactive (furnace or thermal) black, a gel is still formed. Therefore it may be assumed that all carbon blacks can form continuous structures when added in definite, large or small amounts.

Studies of the strength and stability of carbon-rubber gels, based on increasing the time and raising the temperature of extraction, or on using a more active solvent (carbon tetrachloride) showed that more harsh extraction conditions do not result in total disappearance or a substantial decrease of the carbon-rubber gel content. Moreover, it was found that on extraction with carbon tetrachloride or boiling benzene the gel contains less carbon black and more rubber than on extraction with benzene at 20°. Thus the amount of rubber bound with carbon increases in such conditions. Consequently, the action of a more active solvent or increase of temperature intensifies the separation of the carbon black particles from each other, with their subsequent elution, rather than the separation of rubber molecules from carbon particles. The action of carbon tetrachloride becomes more pronounced with decreasing strength of the bonds between the carbon particles (with decreasing tendency to structure formation). Therefore it seems probable that the strength of the bonds between the carbon black particles is one of the main factors in the stability of carbon-rubber gels.

The carbon black structure is reinforced with increasing carbon black content. At the same time the differences between the amounts of carbon-rubber under different extraction conditions decrease. Thus, in mixtures of SKB with 20 parts by weight of channel black the differences between the amounts of gel obtained by extraction with cold and with hot benzene is 11%, whereas with 60 parts by weight there is no longer any difference. This confirms once again that the gel stability depends on the formation of a carbon black structure at high loadings.

It should also be noted that formation of a carbon structure increases the cohesion between the rubber and the carbon. The carbon-rubber gel contains

less carbon and more rubber in the case of structural blacks (channel and acetylene) than in the case of nonstructural blacks (furnace and thermal) (Table IV).

It is at present difficult to say what the nature of the forces is between the carbon black particles and between the carbon and the rubber. Further investigation is also needed of the reasons for the increased strength of the bonds between the rubber and the carbon if a structure is formed. The higher content of gel in synthetic rubbers as compared with natural rubber is of great interest. It is possible that the explanation lies in the larger cohesion forces between the molecules of natural rubber, associated with a tendency to crystallization, hindering adsorption of the rubber molecules on the carbon particles. The higher gel contents of synthetic rubber mixtures probably account for the higher abrasion resistance, reported in the literature, of synthetic rubber vulcanizates in comparison with natural rubber, despite the lower tensile strength of the former.

The results of our investigation show that the formation of a carbon-rubber gel is closely related to formation of carbon networks, i.e., the cohesion between the carbon black particles. The amount of carbon-rubber gel may be a measure of the tendency to carbon structure formation.

It is known that the carbon-rubber gel content determines the abrasion resistance and other properties of a vulcanizate. The fact that the gel content depends on the tendency to carbon structure formation indicates that there is a link between such structures and rubber reinforcement.

SUMMARY

1. Carbon-rubber gels are formed in mixtures containing all the types of carbon black tested (channel, acetylene, nozzle, furnace, thermal) and not only active carbons.

2. The amount of carbon-rubber gel formed depends on the amount of carbon black added. With carbon blacks which readily form continuous carbon structures (channel, acetylene) the amounts of gel are greater than with nonstructural blacks, for the same amount of black added.

3. The amount of gel is greater in synthetic than in natural rubber mixtures.

4. More intense extraction conditions do not cause disappearance of the gel, but increase the amount of bound rubber and decrease the amount of carbon in the gel.

5. The carbon-rubber gels formed from structural carbons contain larger amounts of bound rubber.

6. It is suggested that bond stability between carbon black particles (characterized by the formation of a carbon black structure) is one of the basic causes of carbon-rubber gel formation.

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BASIC PROBLEMS IN THE THEORY OF BOND STRENGTH BETWEEN THE PLIES OF A RUBBER ARTICLE *

G. A. Patrikeev

The problem of ensuring adequate bonding strength between uniform and nonuniform layers in composite vulcanized rubber articles is particularly vital in the production of high grade multi-ply articles for heavy duty (high speeds, high dynamic loading and considerable heat build-up) and also in the production of multi-ply articles from dissimilar compounds based on synthetic rubbers of different structural type. In works practice various methods are known for the production of two-ply and multi-ply composite vulcanized rubber articles, based on plying-up in the hot state (sometimes combined with buffing of the unvulcanized parts and the use of special materials to increase the tackiness of the stocks) and also on the use of solvents and the cementing of the stocks by a cement, sometimes of several types applied in sequence.

Difficult technological tasks arise in the production of composite articles with dissimilar plies based on rubbers of different chemical composition, for instance of natural and sodium butadiene (or chloroprene) or of natural (or butadiene) and butyl rubber. In spite of considerable practical successes, many of the tasks enumerated above remain unsolved, and there is hardly any great hope of success without a previous examination of a number of basic theoretical questions.

A theory of strength has not been worked out even for the most simple case—the stretching of a strip of unloaded vulcanized rubber. There are many questions unstudied, the examination of which must precede the development of a theory of the strength of dissimilar plies in a multi-ply composite rubber article.

Before considering the separate questions we regard it as worthwhile to formulate the general tasks of a theory, keeping within the bounds of the problem under discussion, i.e., bond strength.

According to the minimum requirements, theoretical investigations ought to enable the selection of correct basic (determinant) scientific lines and to facilitate the development of rational methods of investigation, reflecting the essential aspects of the phenomenon being studied.

Of course, major failures and unplanned and wasted labor are often caused by the choice of mistaken lines of investigation or are the outcome of the use of mistaken methods of testing.

According to the maximum requirements, theoretical investigations should lead, on the one hand, to an assessment of the significance of the limiting magnitudes of bond strength between similar or dissimilar plies in composite articles as a function of the strength of the material in the ply, or, on the other hand, to an examination of scientific paths or even to the development of definite methods of ensuring adequate bond strength.

* Translated by R. J. Moseley from '*Prochnost' Svyazi*, 1954, pages 78–86.

As one of the correct and basic lines of scientific work let us take that of the study of covulcanization of dissimilar rubbers (in B. A. Dogadkin's terminology) or of vulcanization in the boundary layer (in the terminology of G. L. Slonimskiĭ). A second line is the study of the mutual penetration of molecules of the polymers in the boundary layer before vulcanization and in the initial stage of vulcanization.

A profoundly erroneous scientific line in our opinion is the study of supplementary electrical forces between the molecules of a polymer in an attempt to assess the bond strength between dissimilar layers of vulcanized rubber. As G. L. Slonimskiĭ said, according to the ideas of B. V. Deryagin, the strength of the homopolar bonds of the molecules of rubber is insufficient, since the experimental values for the energy of formation of an interface in the vulcanized rubber exceed the theoretical magnitude by 2 to 3 orders. In our view, investigations of mythical electrical double bonds, supposed to govern bond strength, are nothing but a waste of time.

To establish the erroneousness of the line of study of supplementary electrical forces as a factor determining bond strength, let us consider some other questions of importance from the theoretical point of view.

1. The expressions "boundary layer" or "interface" are frequently used incorrectly in reports, without qualification, in the sense developed in the physical chemistry of ordinary low molecular compounds. These expressions should on principle not be extended to high molecular compounds. The point is that with high molecular compounds the expression "surface" loses its ordinary meaning after the mutual penetration of the molecules. This is explained by the fact that the condition of the parts of the molecules on the surface of the rubber, in contrast with low molecular compounds, essentially differs neither in the nature of the thermal motion, nor in the nature of the intermolecular forces, from the condition of the parts of molecules in the deep layers. Therefore polymeric substances cannot have perceptible surface tension nor surface pressure in the surface layer. On the other hand, on contact of two surfaces, the mutual penetration of molecules of rubber of one or different types cannot lead to the loss of a strength bond of a transferred part of a molecule with the remaining part, or in other words with a layer of material from which the "end" of a molecule is diffusing. Consequently the phenomena of mutual diffusion of molecules differ fundamentally in low molecular and polymeric compounds. Therefore with the mutual penetration of parts of molecules of rubber from one layer into another layer in contact with it, it is correct to consider and assess the degree of alteration of the surface of molecular contact along with the ordinary surface of geometrical contact. In contrast with the surface of geometrical contact the surface of molecular contact has, on account of the mutual penetration of the molecules, already a transitional character and may be regarded not only as a surface but partly as a volumetric layer. Thus the boundary layer in actual contact of polymeric substances after mutual penetration of the molecules is in effect no longer a surface layer.

The practical outcome of this theoretical exposition is the necessity for assessing the magnitude of the surface of molecular contact. It is quite easy as a first rough approximation to assess the dependence of the relative increase in the area of molecular contact (η) upon the length of an imaginarily straightened part of a polymeric molecule (α) penetrating into the neighboring layer. In the simplest case, for layers of one rubber with penetration of each molecule to a depth α the relative increase in the area of molecular contact may be

assessed from the formula

$$\eta \simeq \frac{2 \cdot \alpha \cdot 10^{-8}}{\sqrt{S}} + 1 \qquad (1)$$

where α is the length of the imaginarily straightened mutually penetrating parts of the molecules of rubber, in Å; S is the effective cross section area of the molecules of rubber, in sq cm; $\sqrt{S}$ is the effective cross sectional dimension of the molecule, in cm. For natural rubber: $S \simeq 25 \cdot 10^{-16}$ sq cm and $\sqrt{S} \simeq 5 \cdot 10^{-8}$ cm.

$$\eta \simeq 0.4\alpha + 1 \qquad (2)$$

By way of example we now give the corresponding figures for the increase in the area of molecular contact for natural rubber as a function of α (in Å), calculated by Equation (2.)

α	η
1.25	1.5
2.50	2.0
5.00	3.0
10.00	5.0
20.00	9.0

If the "ends" of the molecules mutually diffuse in the boundary layer to a depth of 5 to 10Å, i.e., to 4 to 8 links, then the relative increase in the area of molecular contact (for a specimen with a smooth surface of cross section 1 sq cm) reaches, respectively, three or five times the geometrical value. The relative increase in the area of molecular contact will be about half as large if in the boundary layer with similar rubbers only the molecules of one of the rubbers are capable of diffusing.

Even with insignificant mutual penetration of the molecules the area of molecular contact may considerably exceed the area of geometrical contact of the surface in the boundary layer. Nevertheless this question has not so far been studied and therefore we cannot say anything about the degree of actual mutual penetration of the molecules of rubber in the boundary layer.

Unfortunately there are not sufficient data even for an assessment of the relative increase of area of geometrical contact during the roughening of plied-up surfaces. At the same time this task may be comparatively easily solved. In conclusion we will point out that for an assessment for the increase of area of molecular contact considerable importance must attach to the wetting of the contacting surfaces by solvents and bonding agents, since in this case we are creating the conditions for a more considerable mutual penetration of molecules of rubber.

2. G. L. Slonimskiĭ in his report drew attention to the important influence of repeated deformations upon the bond strength of different layers of composite articles. We agree with this. Nevertheless it is necessary to consider that microsurfaces of separation (nuclei of cracks or ply separation) are formed during fatigue with comparatively small deformations of the specimen. There arises therefore the problem of studying local deformations in the boundary layers of multi-ply composite rubber articles. It is agreed to call the usually assessed deformations of the specimen macrodeformations, while the local deformations of the vulcanizate between the particles (or aggregates of particles) of filler are called microdeformations. Accordingly we will draw a distinction

between the stress of the article in the ordinary sense of the word and the microstresses of the vulcanizate.

There is no doubt that the ratio of microdeformations and macrodeformations is determined by the concentration of filler and distribution of particles of filler in the vulcanizate. Up till now this important question has not been studied. At the same time, in the study of microstresses (even comparing the relative deformations of specimens of rubber with different filler content) it is incorrect to compare the physical properties of different compounds with identical macrodeformations of the specimens since in this case the microdeformations and the corresponding microstresses will be all the greater the greater the concentration of the filler in the rubber. In rubbers containing about 30 parts by weight of filler the microdeformations may exceed the corresponding macrodeformations by a factor of two.

As a result of the nonuniformity of microdeformations in the various parts of the vulcanizate we may expect large local overstressing. We must have in mind that the value of the macrodeformations in the vulcanizate on breaking of the testpiece may considerably exceed the magnitude of the relative elongation at break.

An assessment of microdeformations is particularly important in the study of the nature of the reinforcement of rubber by fillers and of the formation of nuclei of cracks and ply separations at elongations which are less than the elongations for break of the specimen.

3. In assessing bond strength between plies of composite articles, it is usual to use small specimens with a 1:1 ratio of height to width. The results thus obtained have been applied to motor tires. At the same time the conditions of deformation of a tire breaker differ considerably from the conditions of deformation of small specimens, since the breaker is a part of a composite tire, and the ratio of width to height in the breaker is greater by 1 to 2 orders than in the specimens under examination. In addition in contrast with the behavior of the breaker, the small specimens of rubber undergo considerable stress, and not only compression. Therefore we must not expect correlation between the bond strength figures in the testing of small specimens of rubber and that of whole tires. In comparing compound formulas we may expect a considerable difference in the behavior of breaker compounds and of specimens, all the greater the more considerable the difference of composition of the compounds.

In this respect the results reported here by A. E. Kornev are particularly questionable, since in tests according the method adopted in his work, the value of the deformation of low moduli rubbers is unjustifiably high in comparison with the deformations of breakers of different modulus.

M. M. Reznikovskiĭ proved the possibility of assessing the failure of specimens through fatigue in very short periods. This method can hardly be regarded as reliable becuase of the possibility of considerable errors in recording the time. In addition, it is doubtful whether we always obtain reproducible results because of too great magnification of the factors leading to failure of the specimens during testing.

4. In assessing bond strength in rubber-fabric articles it is necessary to take into account not only the adhesion of the vulcanized rubber to the filaments of the cord, but also the strength of the rubber enveloping the filaments of the cord. Our experience in working with rubberized glass fiber fabric shows that the strength of the rubber plays the major role in the strength of attachment of the coating and the glass fabric; in the absence of the bond caused by adhesion

the strength of attachment is governed by the effect of keying as a result of the penetration of the glass fabric by the stock during the rubberizing on the calender. In a number of cases it is necessary to consider also that after rubberizing the strength of the fabric is considerably reduced, if we assess the resistance of the rubberized fabrics to tearing. The significant reduction in the tearing resistance of the fabrics is explained by the sharp reduction of the mobility of the filaments relative to one another.

5. G. L. Slonimskiĭ said that according to B. V. Deryagin, in the theoretical assessment of the limiting value of the strength of vulcanized rubber, governed by the homopolar carbon bonds of the rubber molecule (and even in the case of diamond), the strength obtained is lower by 2 to 3 orders than the experimentally determined values. According to the data given, the theoretical value of the energy of the bond is 2.5×10^9 erg/sq cm, while the experimental value is from 10^5 to 10^6 erg/sq cm.

Have we correctly determined the theoretical value of the surface energy, and are the experimental data on the assessment of the surface energy reliable? To answer these questions, which are very important from the theoretical point of view, it is necessary to assess the ratio of the number of elastically deforming carbon bonds and the number of breaking carbon bonds in the mechanical breaking of a vulcanized rubber body (or of a molecule of raw rubber).

Like G. L. Slonimskiĭ, we withholed evaluation of the work on the predominance of the forces of intermolecular interaction, and also withhold consideration of the work on straightening a molecule, and will not consider the processes of relative movements of the molecules preceding elastic stretching of the molecules and their mechanical breakage. Thus the main questions of the theory of elasticity of vulcanized rubber are not considered here, but we do consider, on the other hand, those questions which are completely ignored in the kinetic theory of elasticity as not being of essential importance (according to the erroneous ideas of authors and commentators on the kinetic theory of elasticity). Then for a model it will be necessary to adopt a system of rubber molecules arranged in parallel, not interacting one with another, and elastically stressed; each of these molecules takes $1/N$ of the total stress; in the elastic stretching of each part of the molecule of n carbon atoms there will be expended $1/N$ of the total work of deformation of the imaginary rubber specimen. In this simplified approach the mechanical properties of a body formed by elastically stretched molecules arranged in parallel do not differ from the mechanical properties of a single isolated polymeric molecule. Thus if the cross section of a stretched specimen is taken as unity, while the effective cross section of a molecule is denoted as S

$$N = \frac{1}{S} \tag{3}$$

For simplicity we assume that the original effective cross section S_0 and the actual effective cross section of an elastically stretched molecule S are identical, i.e., $S_0 = S$.

$$Q = N \cdot n \cdot q' \tag{4}$$

$$\frac{Q}{N} = n \cdot q' \tag{4a}$$

$$E = N \cdot E_c \tag{5}$$

$$P = N \cdot S \tag{6}$$

where P is the stress of the specimen, kg/sq cm; Q the work of elastic stretching of a specimen of n carbon atoms in the main chain of each molecule, kg cm; $\bar{q}'$ the average value of the work of elastic stretching, associated with one C—C bond, kg cm; $\bar{q}$ the average value of the work of scission, associated with one C—C bond; $\bar{q}' = \bar{q} - \Delta\bar{q}$; here $\Delta q \ll \bar{q}$; σ = the average value of stress of a polymeric molecule, kg/sq cm; E = elastic modulus of the specimen, kg/sq cm; E_c = the average value of the elastic modulus of a polymeric molecule, kg/sq cm (according to W. Kuhn $E_c \approx 10^6$ kg/sq cm; according to the present author's calculations $E_c \approx 3 \cdot 10^6$ kg/sq cm).

We note that in the elastic stretching of the polymeric molecule of rubber the work is expended in the deformation of valency angles ($109° + \Delta\varphi$) and on the stretching of valency carbon (C—C) bonds. The number of bonds corresponds to the number of carbon atoms in the main chain of the polymeric molecule. The total work U of stretching and scission of N polymeric molecules, the length of which corresponds to n hydrocarbon atoms, is equal to

$$U = (n\bar{q}' + m\Delta q) \cdot N \tag{7}$$

where m is the number of individual scissions of carbon bonds, set up in the scission of the polymeric molecule.

On account of the existence of intermolecular oscillations $\pm\Delta q$ and of the impossibility of effecting further elastic stretching of the polymeric molecule in mechanical scission even at the place of an individual C—C bond, the probability of simultaneous scission of the molecules in two or more places, m, must be insignificantly small. Thus we may take $m = 1$ and $\bar{q} = \bar{q}' = q$ (with an accuracy of up to Δq). Bearing in mind that when the value q is sufficiently great the mechanical scission of the molecules is bound to take place spontaneously and that $\Delta q \ll q$, we find that

$$U = n \cdot q \cdot N \tag{8}$$

or

$$\frac{U}{N} = n \cdot q \tag{8a}$$

From this it follows that

$$q = 7 \cdot 10^{-20} \cdot V \quad \text{kg cm}$$
$$q = 7 \cdot 10^{-14}\, V \quad \text{erg}$$

where V is the energy of dissociation of the C—C bond, in kcal/mole.

Where $V = 50$, $q \approx 3.5 \cdot 10^{-18}$ kg cm or $q \approx 3.5 \cdot 10^{-12}$ erg.

Where $V = 70$, $q \approx 5 \cdot 10^{-18}$ kg cm or $q \approx 5 \cdot 10^{-12}$ erg.

In fact, in the formation of an interface of total area 1 sq cm the surface energy U' is, according to Equations (8) and (3) equal to

$$U' = q\frac{n}{S} \tag{8b}$$

Where $S = 25 \cdot 10^{-16}$ sq cm (for vulcanized natural rubbers)

$$U' = 2 \cdot 10^{-3} \cdot n \quad \text{kg cm/sq cm}$$

or

$$U' = 2 \cdot 10^{3} \cdot n \quad \text{erg/sq cm} \tag{9}$$

We note that the amount of work for fracture of the specimen in testing ordinary specimens for breaking, tearing or ply separation is insignificantly small in comparison with the work for deformation (the work for breaking the strongest rubbers does not exceed 600 to 700 kg cm/cu cm. Incidentally the work for breaking specimens of the best grades of steel is 20 times less). Even with the breaking of the strongest vulcanized rubbers, the work of stretching of a specimen of volume 1 cu cm is almost 2×10^5 greater than that, of formation of a surface of separation of total area 1 sq cm, if we do not consider the microsurfaces of separation formed within the stretched specimen. Therefore, to get commensurate magnitudes of the same order for the work of fracture and the work of preliminary deformation, it is necessary to effect ply separation in very wide, but thin specimens, e.g., of area 100 sq cm with total thickness 10μ.

One gross error, usually tolerated in theoretical assessment of the value of surface energy, is that of leaving out of consideration the fact that deformation must precede the mechanical breakage of the molecules. Thus the value calculated in this way for the surface energy must be increased n times; we must expect n to be very large. According to the same ideas the experimental value of the surface energy $U_{exp} = 10^5$ to 10^6 erg/sq cm is sharply increased. On the other hand, it is more justifiable, on comparing the experimental value of the surface energy with the theoretical, to find the value n

$$n = \frac{U_{exp}}{U_{theoret}} \tag{10}$$

For natural rubber

$$n \approx 0.5 \cdot 10^{-3} U_{exp} \tag{10a}$$

According to data presented by G. L. Slonimskiĭ and calculated according to formula (10a),

where $U_{exp} \approx 10^5$ $n \approx 50$
where $U_{exp} \approx 10^6$ $n \approx 500$

Thus the suggestion of the discrepancy of the experimental and theoretical values of the surface energy is based on a misunderstanding. Therefore we ought not either to talk of such supplementary electrical forces in considering the problem of the stress of polymeric compounds.

In conclusion we note that on the basis of the calculations of W. Kuhn for raw rubber the breaking load, in relation to the effective cross section of the molecules, is approximately 0.2×10^6 kg/sq cm. According to the present author's calculations this value may be greater by one order.

It is not possible to carry out a more accurate calculation on account of the absence of reliable data on the rigidity of polymeric molecules and on the permissible limits of stretching of chemical bonds.

ABRASION OF RUBBER AGAINST ABRASIVE PAPER *

S. B. Ratner and N. V. Melnikova

Abrasion is one of the most important causes of failure of many rubber articles. Therefore, the attention of the testers and investigators centers around the rubber laboratory test-methods for determination of abrasion resistance.

The testing of rubber according to GOST 426-41[1], (ISO)[3] specifies the abrading of the pair of samples against an abrasive paper using the Grasselli type of machine. Some skepticism has been created toward the use of these machines as well as toward the use of sandpaper as abrasive medium, because of the considerable discrepancy of data on abrasion. (We are not considering the question of relationship between the abrasion test data and the actual use performance of an article.) However, our experiments show that without changing the apparatus or the abrasive medium one can greatly increase the accuracy and the reliability of data by decreasing the height of the test sample. Below are presented the data upon which these conclusions are based and which are now being implemented in the new GOST 426-57[2].

The good reproducibility of the results of tests on hundreds of rubbers allowed us to determine an approximate formula connecting the abrasion with other physical and mechanical characteristics of rubber and, therefore, with its composition.

KINETICS OF ABRASION OF RUBBER

Figure 1 (Curves *1*, *4*, *6*, *7*) shows the relationship between the speed of abrasion $\left(\varphi = \frac{\Delta g}{\Delta t}\right)$ and duration of abrasion (t) of various technical rubbers. Each sample of rubber was abraded against the same abrasive paper (monokorund-150). Even though the rubbers differ greatly in the speed with which they abrade, all the curves have similar appearance: each consists of two characteristic parts. In the first part, the speed of abrasion gradually decreases and there is a considerable irregularity of data.

The second part of the curve shows essentially constant speed of abrasion with very little discrepancy of data; this part may be called the stable zone. The tail end of the curve shows that the protruding part of the sample has been worn out. The area underneath each curve denotes the total mass of abraded rubber. This mass is the same for each sample and corresponds to the height of the sample protruding above the frame that holds the sample, $h_0 = 6$ mm.

Figure 1 shows that the stable zone begins after less than one half of the sample has been abraded. Therefore, the first part of the test corresponding to the unstable zone should be devoted to the kind of conditioning or adjustment period without weighing the samples. The weighing should be done at the beginning of the stable zone and abrasion carried on for the desired length of time. The length of time in this zone is unimportant if we relate the loss of

* Translated by Theodore Shevzov from *Kauchuk i Rezina*, Vol. 17, No. 8, 14-21 (1958).

weight to one or the other of time, the number of revolutions, the length of travel, or the work of abrasion.

In spite of the correctness of this concept it is difficult to obtain in practice because of the difficulty in predicting the time of appearance of the stable zone and the differences in time required for the testing of various rubbers. In order to eliminate these difficulties it is necessary to find the cause and the nature of the unstable zone so that in practice the testing could be carried out only in the stable zone.

It is well known that the abrasive paper itself needs stabilization. According to the ISO method the paper is stabilized by abrading the rubber for 20 to 30 minutes. This can also be seen from Figure 1; it may be noted that a high hardness stock (Curve *8*) stabilizes the abrasive much faster than the low hard-

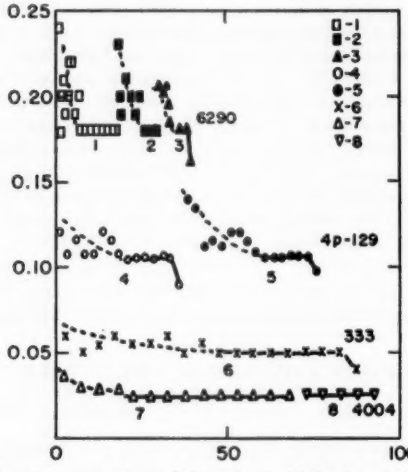

FIG. 1.—The relationship between the speed of abrasion φ with the time of abrasion t. Abscissa; duration of abrasion, minutes. Ordinate; speed of abrasion, cm³/min. *1, 2, 3*—Compound 6290 for conveyor belting: *4, 5, 4p-129* (surface stock); *6-333* (soling grade); *7, 8-4004* (oil resistant); *1, 4, 6, 7*—first series of abrasion tests of a given sample against a given abrasive; *2, 5*—the abrasion of a second sample of the same rubber against the same abrasive sample; *3, 8*—repeated abrasion of rubber samples nos. 1 and 7 against a new piece of abrasive.

ness one (Curve *3*). In the latter case 15 min are sufficient. The basic reason for the existence of the unstable zone lies in the behavior of the rubber (Curves *2, 5*) and not in the behavior of the abrasive paper as the unstable zone appears again when a fresh sample is abraded against a previously stabilized paper.

STANDARDS METHODS OF ABRASION OF RUBBER

Before considering the question of eliminating the unstable zone, let us consider the existing standard methods of abrasion using the Grasselli machine, the samples of rubber and the abrasive paper being the same as in our investigation.

The DuPont method.—As recommended by ISO this method is used in many countries (USA, France, England, etc.). The sample of rubber is fitted tightly (within 0.2 mm), weighed and abraded by not more than 3 mm. This means

TABLE I

COMPARISON (IN PER CENT) OF SPECIFIC ABRASION (V) VS COEFFICIENT OF VARIABILITY (α) OF VARIOUS RUBBERS

Rubber	Test method: GOST 426-41 V	GOST 426-41 α	DuPont method V	DuPont method α	GOST 426-57 V	GOST 426-57 α
4p-129	100	14.4	100	12.7	100	4.7
Conveyor Belting 6290	223	11.8	238	9.3	233	3.0
Sleeve 4004	47	16.2	37	11.3	33	5.2
Footwear	260	10.1	240	9.5	255	3.3
Average		13.1		10.7		4.1

that the whole test is actually carried out in the initial, unstable zone of the curve and discontinued at just about the time when the reproducible and steady abrasion would begin. Inasmuch as the clamping pressure (3.62 kg) is greater than that recommended in GOST (1.6 to 2.6 kg) the force of abrasion and the bend are greater and the stable zone appears even later than in our method. It is clear that such a method is not good and the data are quite irregular (Table I).

GOST 426-41.—The height of the protruding test sample is the same $h_0 = 6$ mm. Because of that, the abrasion period of 5 min was carried out in the unstable zone. Therefore, there was quite a spread in the data and the relationship of the average values of abrasion for various rubbers was variable (Table I). In addition an unstabilized abrasive was used which resulted in still greater irregularlity of data.

The German standard.—This method uses the Schopper's machine. The abrasion of rubber always takes place on the fresh surface of the abrasive. The method is based on the same erroneous ideas as the GOST 426-41; that the variability of results is basically caused by the contamination of the abrasive rather than by the behavior of rubber. Our experiments show, that for all

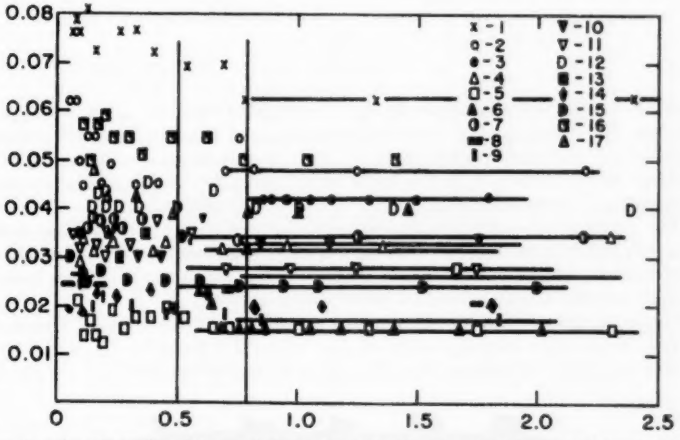

FIG. 2.—The relationship of the speed of abrasion φ/N with resistance to bending $1/f$ (see Table II for identification of compounds and conditions of testing. μ relates to the abrasion in the stable zone; h is determined by weighing during testing).

TABLE II

IDENTIFICATION OF THE RUBBERS AND CONDITIONS OF ABRASION

Compound code	Gum stock	Filler	E kg/cm²	ab cm²	P kg	μ	Abrasive paper
M-33	Polybutadiene	35 Silica	26	2×2	0.325	1.7	Monokorund 150
M-37	Polybutadiene	25 Lampblack	30	2×2	0.325	1.7	Monokorund 150
M-42	Polybutadiene	150 Lampblack	250	2×2	0.325	1.0	Monokorund 150
M-27	Polybutadiene	35 Channelblack	48	2×2	0.325	1.7	Monokorund 150
M-13	SKS-30	22 Channelblack	44	2×2	0.325	1.7	Monokorund 150
4004			200	2×2	0.325	1.0	Monokorund 150
6290			34	2×2	0.325	1.4	Monokorund 150
6290			34	2×0.5	0.324	1.6	Monokorund 150
6290			34	0.5×2	0.325	1.6	Monokorund 150
6290			34	2×2	0.200	1.4	Monokorund 150
6290			34	2×2	0.450	1.5	Monokorund 150
4p 129			55	2×2	0.325	1.4	Monokorund 150
4p 129			55	1×1	0.650	1.5	Monokorund 150
4p 129			55	1.5×1.5	0.325	1.5	Monokorund 150
4p 129			55	2×2	0.650	1.3	Monokorund 150
4p 129			55	2×2	0.325	1.6	General purpose
4p 129			55	2×2	0.325	1.5	K3-100

practical purposes, none of the rubbers change the properties of the abrasive within the stable zone. On the contrary, it is useful to stabilize the abrasive during the initial grinding step (Figure 1); very irregular data are obtained if a nonstabilized abrasive is used.

THE SIGNIFICANCE OF THE HEIGHT AND THE BENDING OF THE TESTPIECE

The ordinate of the Figure 2 shows the speed of abrasion and the abscissa the resistance of the sample toward bending. The resistance toward bending takes into account all the influencing factors.

As is known, deflection f is expressed by

$$f = \frac{Fh^3}{Ea^3b} = \frac{1}{\beta}$$

where F—Force of abrasion causing bending ($F = \mu N$), μ—Coefficient of abrasion, N—Normal load, E—Static modulus of the rubber, h—Protruding height of the testpiece (varies in the process of abrasion), a—Thickness of the testpiece in the direction of the force of abrasion, b—Width of the testpiece, β—Resistance toward bending.

The applicability of this formula to rubber was shown[4] for the case similar to ours in which the bending occurred during displacement. The f in this case characterizes the dislocation of the sample while in motion rather than from the original position during which no deformation existed.

Figure 2 shows that for all samples tested the stable zone of abrasion is located in one area corresponding to f = 1.5 to 2.0 microns, i.e. = 0.5 to 0.8 inverse microns. Consequently, the cause of the irregularity of values is in

FIG. 3.

the bending of the testpiece. Figure 3 shows this bending which causes uneven abrasion of the surface of rubber.

Figure 4 shows that the unstable zone can be significantly decreased by decreasing the protruding part of the testpiece h_0. This is because the uneven abrasion (the unstable zone) is caused by the bending which in turn is caused

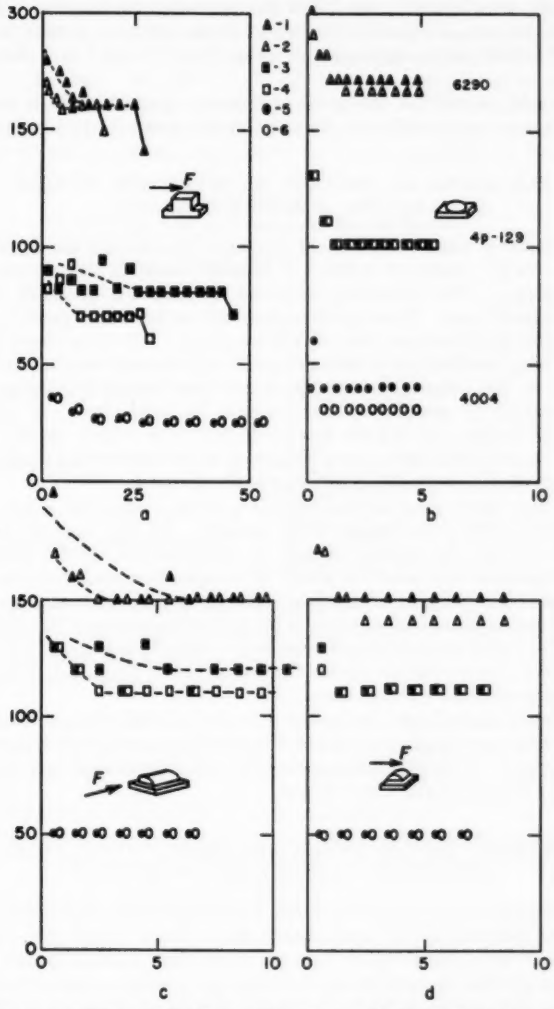

FIG. 4.—Abscissa: duration of abrasion of rubber, minutes. Ordinate: abrasion, mg/min. *1, 3, 5*—tall samples; *2, 4, 6*—short samples; *1, 2*—compound 6290; *3, 4*—4p—129: *5, 6*—4004. a (upper left)—square samples; b (upper right)—round samples; c (lower left)—cylindrical with axle parallel to the force of abrasion; d (lower right)—cylindrical with axle perpendicular to the force of abrasion.

by the force of abrasion. Experience shows that if $a = b = 2$ cm is taken for all the rubbers ($E > 30$ kg/cm^2) the h_0 should be 3–3.5 mm. This result can also be derived from Formula (1). Formula (1) also shows that the same result may be obtained by increasing the thickness of the sample (in the direction of the force of abrasion). This approach would necessitate changing the clamps and obtaining the new molds for curing of the testpieces. In addition, the elongated sample would not follow the curvature of abrasion. Therefore, for practical reasons, decreasing the height of the testpiece is more convenient and the old molds can be employed by using $20 \times 20 \times 2.5$ mm shims in each cavity.

As shown by experience, the speed of abrasion of all the rubbers is such that the h_0 of 3.5 mm is quite sufficient for the abrasion time of 5 to 10 minutes.

THE ANGLE OF CONTACT BETWEEN THE RUBBER AND THE ABRASIVE SURFACE

On the basis of Figure 3 it may be expected that during the bending of the testpiece a certain angle of contact is created between the sample and the abrasive surface. The resulting localized increase in pressure causes an abnormally great wear. The significance of this is variable depending upon the size of the chunks which are torn off the testpiece. The hypothesis of the unstable zone may be checked by two groups of experiments bearing in mind that the change in the height greatly affects the bending of the testpiece. The angle of contact in samples of usual shape (parallelepiped) is also greatly affected. Therefore, by taking the short testpiece which bends little, the stable zone was reached fairly soon (Figure 4, a), as opposed to abrading a tall, square piece when the stable zone was greatly delayed.

A different result may be expected if a similar angle of contact can be achieved regardless of the height of the sample. In this case the moment of appearance of the stable zone should be independent of the height. The rounded testpieces were made in which the angle of contact is constant (close to zero) and is independent of bending. Figure 4, b shows that the kinetics of abrasion of the rounded test-samples is indeed independent of the height of the sample. The same is observed on abrading a cylindrical sample when the axle of the cylinder is perpendicular to the force of abrasion (Figure 4, d) because the angle of contact is also close to zero.

It has been shown that the unstable zone (i.e., uneven and fast wear) is caused by the large angle of contact between the sample of rubber and the abrasive surface. This information may be useful in designing rubber goods, among other things, in tire tread design.

THE RELATIONSHIP BETWEEN ABRASION AND PHYSICAL AND MECHANICAL PROPERTIES OF RUBBER

Numerous attempts have been made to establish the relationship between abrasion and physical (and mechanical) properties of rubber[5–11]. Empirical formulas have been found which held true only for certain rubbers. Having found a reproducible method of determining the abrasion resistance of rubber, we have also attempted to find the relationship of abrasion to other physical properties while varying the composition and the properties of compound over a wide range.

We have derived the formula:

$$\Delta V = K\frac{\mu\eta}{\sigma} = C\frac{N}{\sigma}\mu\eta t \qquad (2)$$

where ΔV—Decrease of volume of rubber by abrasion over time t. If $t = 5$ minutes, ΔV corresponds to the value (in cm³) calculated through Δg in GOST 426-57. μ—Coefficient of abrasion of rubber (this value is also determined in GOST 426-57). N—Normal load on the testpiece (according to GOST 426-57, as a rule $N = 2.6$ kg). η—100 $(1 - h/h_0)$, e.g., per cent loss of height in the sample when determining the elasticity of rubber by GOST 6950-54. σ—Tensile strength as defined in GOST 270-53. C—Abrasive constant which describes the abrasive ability of the paper; we have found that for monokorund

TABLE III

COMPARISON OF THE OPTIMUM FILLER LOADING FOR σ AND FOR $\frac{1}{\Delta V}$

Gum stock	Filler	Optimum filler loading, phr: For σ	Optimum filler loading, phr: For $\frac{1}{\Delta V}$
Polybutadiene (SKB)	Channel black	75	75
	Silica	75	75
	Lamp black	100	105
	Clay	100	105
SBR (SKS-30AM)	Channel black	65	75
	Lamp black	100	100
	Furnace black	75	60
	Thermal black	100	100
Polychloroprene rubber (Nairit)	Channel black	45	35
	Furnace black	65	75

$= 150$ $C = 35$ mm³/min (when used according to GOST 344-57). K—Abrasive constant under the standard test conditions (GOST 426-57) $N = 2.6$ kg; $t = 5$ min; then $K = 0.4$ kg/cm³.

The basis for the formula is as follows:

1) Proportionality between ΔV and t can be seen from Figures 1 and 2 which show that in the stable zone the speed of abrasion is constant.

2) Proportionality between ΔV and N was shown[12]; this is also confirmed in Figure 2.

3) Proportionality between ΔV and μ was established[13].

4) Inverse proportionality of ΔV and σ is logical because a stronger rubber abrades less. In addition we have found that the optimum filler loading practically coincides for σ and $\frac{1}{\Delta V}$ (see Table III).

5) Proportionality of ΔV and η is also logical because the greater the mechanical loss (absorbed energy), the greater the abrasion.

Quantitatively Formula (2) is confirmed in Figure 5 which shows the data for 150 rubber compounds representing various gum stocks, filler loadings, plasticizers, state of cures and agings.

The mean deviation from the straight line (variation of constant K) is 20%.

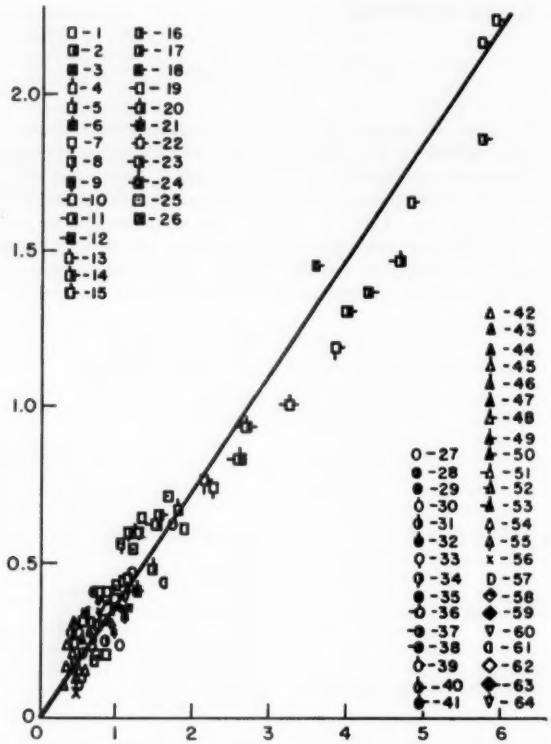

FIG. 5.—The relationship of wear (ΔV) with abrasion (μ), hysteresis (η) and tensile strength (σ) of rubber
Ordinate: The wear of rubber in 5 minutes, cm³. Abscissa: $\frac{\mu\eta}{\sigma}$, cm²/kg.

The value of specific abrasion V may be calculated from the formula:

$$V = \frac{\Delta V}{W} = A\,\frac{\eta}{\sigma} \tag{3}$$

where W is the work of abrasion.

TABLE IV

COMPARISON OF SPECIFIC ABRASION V OF VARIOUS COMPOUNDS AGAINST ABRASIVE PAPERS* 3/100 AND K3-100

Compound	V_1 (3/100)	V_2 (K3-100)	$\frac{V_2}{V_1}$
Conveyor belting	1250	957	0.76
Sleeve	590	428	0.73
Footwear	1075	793	0.74
Tire tread	990	750	0.76
Average			0.75

* The data represent average values of 100 runs of every compound against each of the papers.

Assuming σ in kg/cm^2 and η in per cent, and determining (from the above data) that for the abrasive paper monokorund 150, $A = 700$; we obtain V in cm^3/kilowatt-hours.

Inasmuch as the values for η and σ depend only upon the rubber compound, the correlation of V values for various rubbers over various abraders should be the same. Table IV shows that this conclusion is valid (abrasive paper 3/100 abrades various rubbers one third more than the paper K3-100).

Table V shows that this conclusion remains valid provided there is no fundamental change in the abrasive medium which may change the mechanism of abrasion.

TABLE V

COMPARISON OF SPECIFIC ABRASION V OF TWO COMPOUNDS OVER VARIOUS ABRASIVES

Description of abrasive papers			
Abrasive	Grain*	% retained on 100 mesh screen	V_1**/V_2
Silica	180	0.0	1.46
Electrokorund (regular)	201	4.0	1.26
Electrokorund (coarse)	925	9.8	1.23

* Grams per m^2.
** V_1—Abrasion of conveyor belting stock No. 6290, V_2—Abrasion of tire tread stock 4p-129.
The data represent average values of 50 runs of each compound against every abrasive paper.

The correlation of V is the same (1.25) when two carborundum papers are used even though their grain is different. Using sandpaper the correlation of V is significantly different (1.46).

SUPPLEMENTARY REMARKS

Figure 4 shows that the speed of abrasion of round or cylindrical samples becomes constant after a certain, usually short (1–2 min) period of time. This is true of all the rubbers and is independent of the height of the sample; consequently, the reason for the initial irregularity of abrasion is not the bending of the sample but rather its shape. Indeed, in the process of abrasion of rounded or cylindrical samples while retaining constant the normal load N, the specific pressure P is very great initially; this increases the distance between the crests of the abrading sample which in turn determines[14] the speed of abrasion. Figure 4 shows that, theoretically, the rounded or cylindrical testpiece makes the most suitable sample. However, in practice, these are difficult to prepare from the finished articles.

It is interesting to note that the cylindrical sample, even when its axis is parallel to the force of abrasion, gives more consistent data than the square sample. An analogous phenomenon is observed when the surface perpendicular to the force of abrasion has a triangular shape. Apparently, this is connected with the socalled angle of incline.

It should be pointed out that the speed of abrasion is also stabilized after a certain period of time on the Dunlop-Lambourn abrader. The authors[15] tiein this time with the process of centering and matching between the sample and the abrasive disc. Unfortunately, their work does not list the evidences supporting this explanation.

Finally, let us consider a practical and convenient approach when trying to establish the fine differences of abrasion among several types of compounds.

In this case the samples of the various rubbers may be abraded (in their stable zone) using the same piece of abrasive paper. The change in the abrading ability of the paper can be noted and allowed for by alternation of the samples and through the change in the coefficient of friction which varies with the rate of wear[13].

CONCLUSIONS

1. Studying the kinetics of abrasion on the Grasselli machine, we discover a new phenomenon, the appearance of the stable zone of abrasion.

2. The stable zone is independent of the clogging of the abrasive; it is characteristic of the process of abrasion; it exists despite the widely held opinion that the abrasion data are necessarily highly scattered.

3. The reason for the delay of the stable zone, encountered in practice, is the high degree of bending of the testpiece.

4. The high degree of bending of the testpiece creates a large angle of contact between the rubber and the abrasive surface, which causes the increase in pressure. The angle of contact can be decreased by rounding the surface of the testpiece (e.g., to give a semisphere or semicylinder).

5. Standard methods (GOST 426-41, ISO) provide for the testing of rectangular samples in the unstable zone.

6. The unstable zone can be eliminated completely by shortening the testpieces (up to $h_0 = 3.5$ mm) which sharply decreases the scattering of the data.

7. The testing of abrasion should be carried out using a previously stabilized abrasive paper, for example, during the initial grinding of the rubber.

8. By abrading in the stable zone and using the same piece of abrasive paper, one can determine small differences (several per cent) in abrasion between various compounds.

9. The abrasion of rubber may be related to the friction μ, hysteresis η and tensile strength σ, by approximate formulas.

$$\Delta V = K\frac{\mu\eta}{\sigma}; \quad V = A\frac{\eta}{\sigma}$$

where the values of K and A characterize only the abrading ability of the paper. By changing the compound and consequently its physical and mechanical properties (σ, η, μ), one can vary the abrasion resistance. Other empirical formulas can be found which would relate the abrasion of rubber to other properties such as the elongation, tear resistance, etc.

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CHOICE OF RESILIENT MATERIALS FOR ANTI-VIBRATION MOUNTINGS *

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REPRESENTATION OF THE MECHANICAL PROPERTIES OF A VISCOELASTIC MATERIAL

The relation existing between small values of stress and strain in a linear viscoelastic medium can be most generally represented by a linear partial differential equation of arbitrary order. This equation becomes algebraic when both stress and strain very sinusoidally with time, because the operator

$$\partial^n/\partial t^n = (j\omega)^n \tag{1}$$

where t is time, ω is angular frequency, and $j = (-1)^{\frac{1}{2}}$. The ratio of stress to strain in a viscoelastic material can therefore be expressed as a complex quantity[1], and the mechanical properties of the material represented not by a real, but by a complex "elastic" modulus, possessing real and imaginary parts that are both, in general, functions of frequency. The damping factor of the material is defined as the ratio of the imaginary to the real part of the modulus, and is analogous to the reciprocal of the magnification Q which is employed in electrical circuit theory to describe the ratio of an inductive reactance to a resistance.

GENERAL TRANSMISSIBILITY EQUATION

Figure 1 (a) diagrammatically shows an item of mass M resiliently mounted on an infinitely massive foundation, and sinusoidally vibrating at an angular frequency ω. The item is said to be simply mounted, and the item plus mounting is known as the simple mounting system[2]. Let the resilient isolator possess a complex modulus $\bar{E}$, with a real part E' and an imaginary part E''. Transmissibility T is defined as that fraction of the force exciting the mounted item which is transmitted to the foundation, and is given by the relation:

$$T^2 = \left|\frac{F_2}{F_1}\right|^2 = (1 + \delta^2) \Big/ \left[\left(1 - \frac{\omega^2 M}{kE'}\right)^2 + \delta^2\right] \tag{2}$$

where the damping factor $\delta = E''/E'$. The quantity k is a constant determined solely by the mount geometry, for example, when the mount possesses uniform cross section, k is equal to the ratio of the cross sectional area to the mount thickness.

In practice, the quantities E' and δ are not constant, but functions of frequency. Thus, suppose that the real part of the modulus $E' = E_\omega$, and the damping factor $\delta = \delta_\omega$ at an angular frequency ω, and suppose that the reso-

* Reprinted from the *British Journal of Applied Physics*, Vol. 9, pages 461–469, December 1958. The present address of the author is The University of Michigan Research Institute, Ann Arbor, Michigan.

nance of the mounting system occurs at an angular frequency ω_0 (Figure 1*b*), when $E' = E_0$, such that $\omega_0^2 = kE_0/M$. (Transmissibility is presented here on a decibel scale; thus, a force ratio equal to T appears on a decibel scale as 20 $\log_{10}(T)$ decibels.) It then follows that the quantity

$$\frac{\omega^2 M}{kE'} = \frac{\omega^2}{\omega_0^2} \cdot \frac{E_0}{E_\omega} \tag{3}$$

so that if the frequency ratio ω/ω_0 is equal to x, Equation (2) becomes:

$$T^2 = \frac{(1 + \delta_\omega^2)}{[1 - x^2(E_0/E_\omega)]^2 + \delta_\omega^2} \tag{4}$$

From this equation the transmissibility of any linear rubberlike material can be derived when the variation with frequency of the dynamic modulus (namely, that of the real part of the complex modulus) and damping factor possessed by the material are inserted.

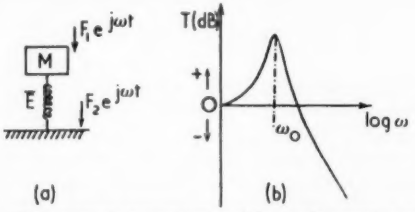


FIG. 1.—Diagrammatic representation of the simple mounting system.

CHOICE OF ISOLATING MATERIAL

The transmissibility of an anti-vibration mounting should be small at all frequencies which it is required to isolate, and the resilient mount material should therefore be chosen to provide:

(i) a low natural mounting frequency ω_0;
(ii) a low transmissibility at resonance; and
(iii) a rapid decrease of the transmitted force with increase in frequency above ω_0.

A low natural frequency can be obtained by employing a mount of suitably low stiffness (or by increasing the mass of the mounted item). The use of a high damping mount material ensures that the resonant transmissibility is small and, in addition, when the vibrating item is resiliently mounted on a nonrigid foundation, it is valuable in suppressing the natural modes of vibration of the foundation[2]. The decrease in the transmitted force at frequencies above ω_0 varies considerably with the rubberlike material employed in the mounting. The comparative behavior of different resilient materials is discussed in later sections.

APPLICATION OF THE GENERAL TRANSMISSIBILITY EQUATION

Damping of the solid type.—A number of materials, including natural rubber, are found in practice to possess a damping factor which is largely independent

of frequency. The real and imaginary parts of the complex elastic moduli possessed by these materials, E' and E'' respectively, must therefore be approximately constant, or show a similar frequency dependence. Such materials are said to possess solid-type damping.

The mechanical behavior of a linear viscoelastic material subject to sinusoidal variations of stress and strain can be represented by a parallel spring and dashpot which will, in general, possess both frequency-dependent modulus of elasticity (E), and viscosity coefficient (η) (Figure 2). For sinusoidal excitation the complex ratio of stress to strain in such an element is equal to $E + j\omega\eta$. The real part of the complex modulus (E') possessed by the material is therefore represented by E, and the damping factor (E''/E') by $\omega\eta/E$.

It is sometimes possible to describe approximately the behavior of a rubber-like material by assuming either (i) that E' and E'' are constant, or (ii) that E' and E'' are both directly proportional to frequency.

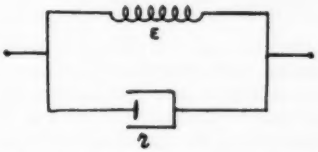


FIG. 2.—Representation of linear viscoelastic material.

(i) Both E' and E'' constant. Namely, E constant and δ constant (hence, η inversely proportional to frequency). Equation (4) becomes:

$$T^2 = \frac{1 + \delta^2}{(1 - x^2)^2 + \delta^2} \tag{5}$$

At frequencies well above the natural mounting frequency, T is therefore inversely proportional to the square of the frequency, that is, T decreases at 12dB/octave. The transmissibility of a resilient isolator possessing constant modulus and damping factor is shown as a function of frequency in Figures 3 and 4. The damping factor is assigned values 0.1 and 1, which respectively typify the damping possessed by natural and some high damping rubbers.

(ii) Both E' and E'' proportional to frequency. Namely, E proportional to frequency, and δ constant (hence, η constant). Equation (4) becomes:

$$T^2 = \frac{1 + \delta^2}{(1 - x)^2 + \delta^2} \tag{6}$$

since

$$E_0/E_\omega = \omega_0/\omega$$

Therefore, at frequencies well above the natural frequency, T is now inversely proportional to frequency, that is, T decreases at 6 dB/octave. The transmissibility of an isolator possessing a constant damping factor, and an elastic modulus directly proportional to frequency is shown as a function of frequency in Figures 3 and 4. The damping factor is again assigned the values 0.1 and 1.

Damping of the viscous type.—This is the type of damping most commonly discussed in literature concerned with vibration isolation. The elastic modulus

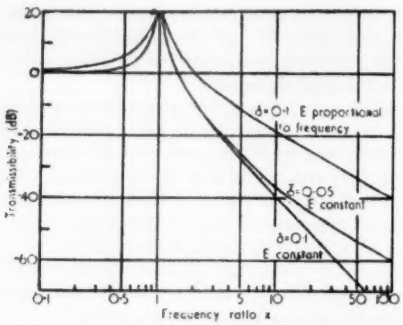


FIG. 3.—The transmissibility of a parallel spring-dashpot element in the simple mounting system. Damping factor $\delta = 0.1$.

E and the viscosity coefficient η are considered constant, so that the damping factor δ is directly proportional to frequency.

In the case of viscous damping it is found convenient to define a damping ratio $\bar{\delta}$ which is characteristic of the mounting system as a whole. The damping ratio is defined as the ratio of the viscosity coefficient actually possessed by the isolator and that required to damp the system critically. It can be shown[3] that $\bar{\delta} = \omega_0\eta/2E$. The damping factor, which previously has been shown equal to $\omega\eta/E$, can therefore be replaced by the quantity $2(\omega/\omega_0)\bar{\delta}$. Equation (4) then becomes:

$$T^2 = \frac{1 + (2x\bar{\delta})^2}{(1 - x^2)^2 + (2x\bar{\delta})^2} \tag{7}$$

Since E and η are considered independent of frequency, the damping ratio $\bar{\delta}$ will be constant. At frequencies well above the natural frequency T is therefore inversely proportional to frequency, that is, T decreases at 6 dB/octave. Since the increase in high frequency isolation is now less rapid than when the mount possessed solid-type damping (with constant modulus E), it may be concluded (Section 3) that a vibration isolator should preferably possess damping of the

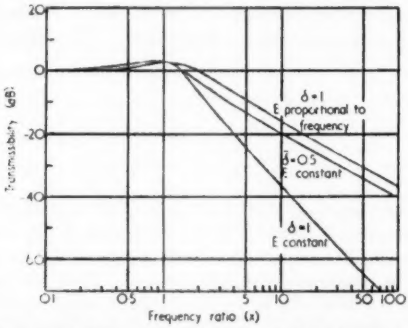


FIG. 4.—The transmissibility of a parallel spring-dashpot element in the simple mounting system. Damping factor $\delta = 1.0$.

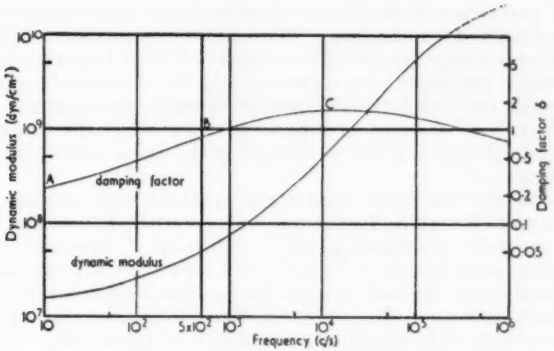


FIG. 5.—The damping factor and dynamic modulus of SBR rubber at 20° C. (Due to Ivey, Mrowca, and Guth.)

latter type. The transmissibility of an isolator assumed to possess constant elastic modulus and viscosity coefficient is shown as a function of frequency in Figures 3 and 4. The damping ratio is assigned the values 0.05 and 0.5.

The relaxation of rubberlike materials.—Figure 5 shows the variation of the dynamic modulus and damping factor exhibited by the synthetic rubber SBR at room temperature[4]. The frequency at which the damping factor possesses a maximum value is known here as the transition frequency; a rapid increase in modulus with frequency occurs in this region. The frequency variation of the dynamic modulus and damping factor in any viscoelastic material are of an essentially similar nature to the curves shown in Figure 5.

At room temperature the transition frequency of natural and other low damping rubbers occurs at very high frequencies, so that over the frequency range normally of interest in vibration isolation (namely, well below the transition frequency) the damping factor is small, and, in fact, both the damping factor and the dynamic modulus may be considered sensibly independent of frequency. Figure 6 shows the experimentally determined transm ssibility of a natural rubber specimen in the simple mounting system. The specimen con-

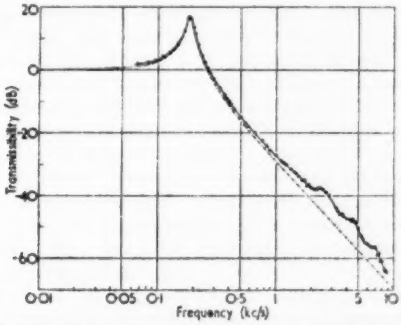


FIG. 6.—The transmissibility of natural rubber in the simple mounting system. Temperature 19° C. Mounts contain forty parts channel black in one hundred parts natural rubber. Broken curve calculated assuming constant damping factor δ and modulus E.

tains forty parts channel black in one hundred parts natural rubber, and is 0.5 in. long and 0.875 in. in diameter. These results are compared with the theoretical transmissibility (broken curve) calculated from Equation (5). Values of the equation parameters are chosen so that the theoretical transmissibility coincides with the experimental curve at the observed resonant frequency. "Wave effects" are observed at high frequencies[5] when the mount length is equal to, or greater than, a half wavelength of the elastic wave passing through the mounting.

In general, the transition frequency of synthetic high-damping rubberlike materials is much lower than for natural rubber or SBR, occurring at frequencies which are normally of interest at room temperature. The damping factor is therefore large over a range of frequencies within which the natural mounting frequency will occur, and may be considered approximately constant, while the dynamic modulus is approximately proportional to frequency. Figure 7 shows the experimentally determined transmissibility of Hycar 1001 (a butadiene/acrylonitrile copolymer) in the simple mounting system, for a specimen 0.375 in. long and 0.75 in. in diameter. These results are compared with the theoret-

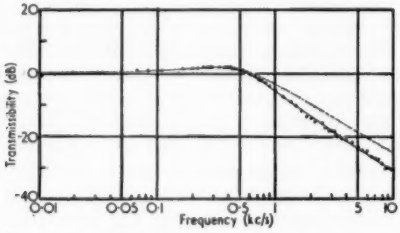


FIG. 7.—The transmissibility of Hycar 1001 in the simple mounting system. Temperature 16.5° C. Broken curve calculated assuming constant damping factor δ and frequency proportional modulus E.

ical transmissibility (broken curve) calculated from Equation (6). Values of the equation parameters are again chosen so that the theoretical and experimental curves coincide at the observed resonant frequency.

Substitution in the general transmissibility equation of the dynamic modulus and damping factor possessed by a rubberlike material.—The frequency dependence of the elastic modulus and the damping factor possessed by rubberlike materials is typified by that of SBR rubber shown in Figure 5. The curves of this figure are used here to determine how the vibration isolation provided by high damping rubbers is related to the frequency variation of their mechanical properties. Thus, the form of the isolation afforded by relatively low, high, and very high damping rubbers is apparent when the frequencies A, B and C (Figure 5) are taken as unity on a relative frequency scale, and the resonant frequency of a vibrating item mounted on each "material" made to coincide with the corresponding unit frequency. The quantity E_0 is equated to the value of the dynamic modulus at the frequencies A, B and C, the corresponding values of the damping factor being 0.23, 0.82 and 1.60. The transmissibility of the three mounting systems can be calculated from the general equation, Equation (4). The calculated transmissibility is presented in Figure 8. Curves a, b and c correspond to the resonance of the mounted item at A, B and C.

The general transmissibility equation shows that at very high frequencies

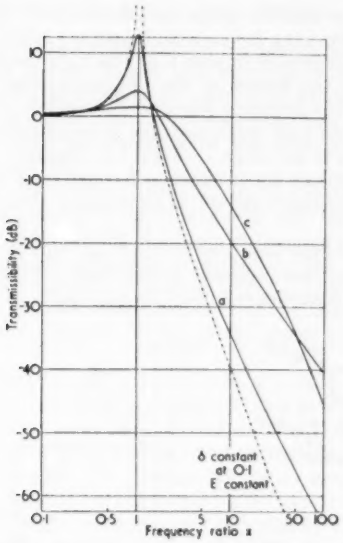


FIG. 8.—Calculated transmissibility curves for a rubberlike material. Curve (*a*) derived from the low damping region of the SBR relaxation curve, Curve (*b*) intermediate damping, and Curve (*c*) high damping region.

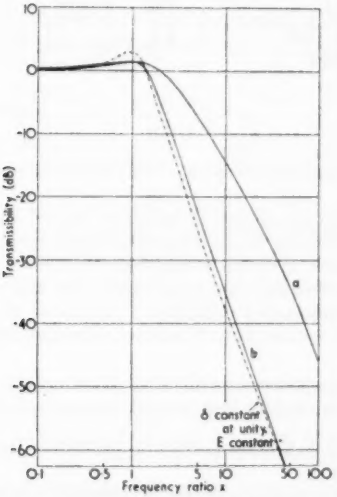


FIG. 9.—Showing how the rapid increase in modulus about the transition frequency is responsible for the loss in high frequency isolation. Curve (*a*) is identical with Curve (*c*) of Figure 8, Curve (*b*) is derived from Curve (*c*) assuming that the dynamic modulus is independent of frequency.

the transmissibility is sensibly proportional to $(1/x^2)(E_\omega/E_0)$, provided that the variation of the damping factor with frequency is not large. Any increase in modulus E_ω with frequency implies that the high frequency transmissibility ceases to decrease as the square of the frequency, that is, at 12 dB/octave. Since for natural and low damping rubbers, E_ω does not increase with frequency to any great extent, the high frequency loss in isolation, or the departure from 12 dB/octave fall-off, is not large. (Figure 6; Figure 8, Curve *a*.) For high damping rubbers, however, the increase in E_ω with frequency, and the resulting departure from 12 dB/octave fall-off, is appreciable (Figure 7; Figure 8, Curve *c*).

High damping rubbers may therefore be undesirable mount materials because their elastic modulus increases greatly with frequency, and not because of their inherent high damping as commonly supposed. Figure 9 illustrates how

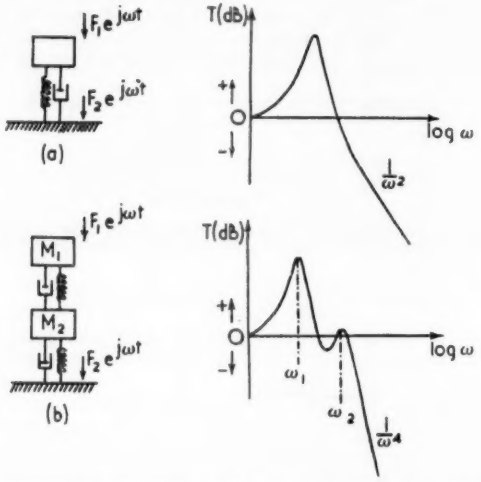


FIG. 10.—Diagrammatic representation of the simple and compound mounting systems.

closely the loss in high frequency isolation is related to the rapid increase in modulus at frequencies near to the transition frequency. Curve *a* is identical with Curve *c* of Figure 8; Curve *b* is derived from Curve *c* of Figure 8 assuming that the modulus is frequency-independent, but with the variation of the damping factor with frequency unaltered. It is seen that virtually the entire departure from 12 dB/octave fall-off is due to the frequency dependence of the dynamic modulus.

Criteria defining a good resilient vibration isolator.—It can be concluded from Figure 9 that a good anti-vibration mount material should:

(i) possess a large damping factor—to provide a low resonant transmissibility;
(ii) be free from any major increase in dynamic modulus or damping factor with frequency—to ensure a rapid decrease of transmissibility with increase in frequency above resonance.

COMPOUND MOUNTING SYSTEM

Introduction.—It has been shown that the high frequency isolation afforded by the simple mounting system (Figure 10*a*) increases as the square of the frequency, providing that the damping factor and elastic modulus of the mounting are constant. Figure 6 shows that the transmissibility calculated for such conditions is in reasonable agreement with the experimentally determined transmissibility of natural rubber.

Isolation superior to that of the simple system can be obtained above a certain frequency by introducing a secondary mass into the resilient mounting, as M_2 in Figure 10(*b*), to form what is known as the compound mounting system[2]. The form of the transmissibility possessed by the compound system is shown as a function of frequency in Figure 10(*b*). This system possesses a secondary as well as a primary resonance, but above the secondary resonant frequency ω_2, the isolation increases as the fourth power of the frequency, that is, at 24 dB/octave.

Properties and applications of the compound mounting system.—The mass ratio β is defined as the ratio of the secondary and principal masses M_2/M_1 (Figure 10*b*). For a given mass ratio, optimum conditions are realized when the frequency separation of the primary and secondary resonances is least. This occurs when the ratio θ of the lower to the upper mount stiffness is equal to $(1 + \beta)$, providing that the mount damping factors are negligible. Under these conditions the ratio of the secondary and primary resonant frequencies, namely, ω_2/ω_1 (Figure 10*b*) is given by the relation:

$$\frac{\omega_2^2}{\omega_1^2} = \frac{(1+\beta) + (1+\beta)^{\frac{1}{2}}}{(1+\beta) - (1+\beta)^{\frac{1}{2}}} \tag{8}$$

Providing that the mass ratio is small and the mount damping factors remain negligible, optimum conditions are practically realized when the mount stiffness ratio is equal to unity. For example:

	β	0.1	0.2	0.5	1.0
$\theta = (1 + \beta)$	ω_2/ω_1	6.48	4.69	3.15	2.41
$\theta = 1$	ω_2/ω_1	6.49	4.71	3.23	2.62

At frequencies above the secondary resonance, the compound system affords greater isolation than the simple system, the difference in isolation increasing at 12 dB/octave. The compound system can, therefore, be advantageously employed when especially good isolation is required. The secondary resonance is an undesirable feature of this system, but it can be suppressed by suitably high mount damping, in common with the primary resonance.

The compound system is of especial value in mitigating the isolation loss always occurring at the natural frequencies possessed by nonrigid foundations[2]. For example, the resonant modes of vibration excited in the structural girders supporting a vibrating machine, or the resonance of a rigid machine foundation with the "elastic" sub-soil (plus its associated "mass") beneath it[6]. The isolation loss at the natural frequencies of such relatively undamped foundations is normally considerable[2,6].

RESULTS OF TRANSMISSIBILITY MEASUREMENTS ON RUBBERLIKE MATERIALS IN THE SIMPLE AND COMPOUND MOUNTING SYSTEMS

THE SIMPLE MOUNTING SYSTEM

The transmissibility of natural rubber.—Results of transmissibility measurements on natural rubber at 19° C have been previously presented in Figure 6, for a specimen containing forty parts channel black in one hundred parts natural rubber.

The damping factor of the rubber at the resonant frequency is equal to 0.14. The close correspondence of the experimental and theoretical transmissibility curves below the first standing wave frequency indicates that the increase in elastic modulus of the rubber with frequency is not large.

It has been shown[5] that the first standing wave resonance occurs when the mount length is equal to a half wavelength of the elastic wave passing through the mounting, and that other wave resonances occur at integral multiples of this frequency. Inspection of Figure 6 shows that if the first resonant wave frequency is taken as 2.3 kc/s, then the second and third wave resonances do occur at, or in the immediate neighborhood of 4.6 and 6.9 kc/s.

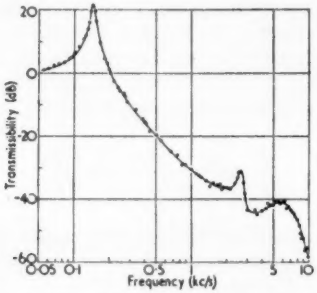


FIG. 11.—The transmissibility of Heveaplus M-G in the simple mounting system. Temperature 21.5° C.

The transmissibility of Hycar 1001.—Results of transmissibility measurements on Hycar 1001 at 16.5° C have previously been presented in Figure 7.

Hycar 1001 possesses a large damping factor of the order unity, which together with the dynamic modulus is very sensitive to variations in temperature. The transmissibility at resonance is heavily suppressed by this high damping. At frequencies above resonance, the isolation afforded by the Hycar increases at 8 dB/octave only, indicating that the increase in modulus with frequency is appreciable.

The transmissibility of Heveaplus M-G.—Heveaplus M-G[1] is a rubber free from conventional fillers such as carbon black, which derives its reinforcement from polymethyl methacrylate. It is prepared by polymerizing polymethyl methacrylate in rubber latex to give a graft polymer in which the rubber molecules have attached side chains of methyl methacrylate.

Under low amplitude vibration Heveaplus M-G possesses a much lower dynamic modulus and damping factor than a black-reinforced compound with similar static properties.

The transmissibility of Heveaplus M-G at 21.5° C is shown in Figure 11. The specimen contains five per cent methyl methacrylate in the total polymer.

It is 0.438 in. long and .0375 in. in diameter. The transmissibility curve reflects the low damping characteristics of the polymer, namely, a relatively sharp resonance (damping factor $\delta = 0.08$ at the resonant frequency), a rapid decrease in transmissibility with frequency above resonance, and pronounced wave effects at high frequencies. The standing wave resonances appear to be less regular in nature than those of the natural rubber specimen previously discussed. The first wave resonance is clearly defined, and occurs at 2.66 kc/s. There is no evidence of equally well defined wave resonances at 5.32 and 7.98 kc/s, although a broad maximum does exist in the region of 5.5 kc/s.

The transmissibility of castor oil urethane.—Castor oil urethanes are produced by crosslinking castor oil with a diisocyanate, and are characterized by their flexibility and high damping factor[8].

The transmissibility of castor oil urethane at 22° C is shown in Figure 12. The specimen contains forty parts diisocyanate in one hundred parts castor oil. It is 0.375 in. long and 0.813 in. in diameter.

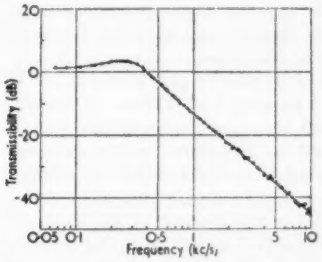


FIG. 12.—The transmissibility of castor oil urethane in the simple mounting system. Temperature 22° C. Mounts contain forty parts diisocyanate in one hundred parts castor oil.

The damping factor at the resonant fequency is equal to 0.89. Above resonance the isolation afforded by the castor oil urethane increases with frequency at 10 dB/octave, more rapidly than normally found for a material (for example, Hycar 1001) with such a high damping factor.

The transmissibility of irradiated polythene.—High polymers are essentially composed of chains of large numbers of monomeric units; the main chain may not always be linear, and branched side chains may be present. Exposure to nuclear irradiation either degrades the main or side chains, or produces crosslinks between them[9,10].

Polythene is readily crosslinked, primary bonds forming between adjacent carbon atoms. The degree of crosslinking is dependent on the radiation dose. At room temperature polythene is largely crystalline and, although crosslinking occurs when polythene is irradiated, the crystallinity it posseses is destroyed. Crosslinking increases the elastic modulus of the polymer, but the decrease in crystallinity is reflected as a decrease in modulus.

The reduction in modulus at room temperature as the radiation dose is increased from zero to eight units is due to the decrease in crystallinity outweighing the effect of the crosslinking produced by the irradiation. (One radiation unit is defined as an integrated flux of 10^{17} slow neutrons per square centimeter, plus associated fast neutrons and γ-rays.) Above eight units the modulus increases as the degree of crosslinking increases still further, and the material becomes more rigid and eventually brittle and glasslike.

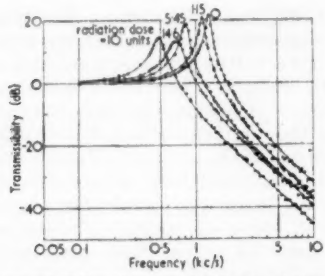


FIG. 13.—The transmissibility of neutron irradiated polythene in the simple mounting system. Temperature 18° C.

The damping factor of polythene exhibits a maximum, and the elastic modulus a minimum value, after approximately eight units of irradiation. Both the damping factor and the modulus are extremely temperature and frequency sensitive for this dosage, and at room temperature the polythene exhibits typically rubberlike behavior.

The transmissibility of irradiated polythene at 18° C is shown in Figure 13. The specimens are 0.375 in. long and 0.75 in. in diameter. The nature of the transmissibility curves at resonance reflects the behavior of the modulus and damping factor possessed by irradiated polythene described above. At first sight it would be expected that the resonant transmissibility of polythene at 14.6 units of irradiation would be greater than at ten units. That this is not so may probably be ascribed to the increase of the damping factor with frequency being greater than the reduction of the damping factor that occurs as the polythene moves further towards the brittle or glasslike state.

THE COMPOUND MOUNTING SYSTEM

The transmissibility of natural rubber.—Results of transmissibility measurements on natural rubber specimens in the compound system at 19° C are presented in Figure 14, together with the transmissibility of an identical specimen in the simple system, shown previously in Figure 6. The test specimens contain forty parts channel black in one hundred parts natural rubber.

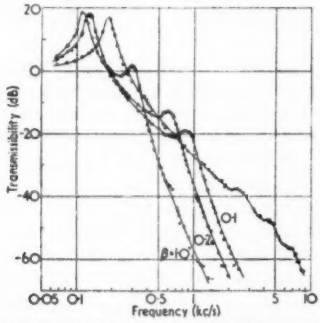


FIG. 14.—The transmissibility of natural rubber in the simple and compound mounting systems. Temperature 19° C. Mounts contain forty parts channel black in one hundred parts natural rubber.

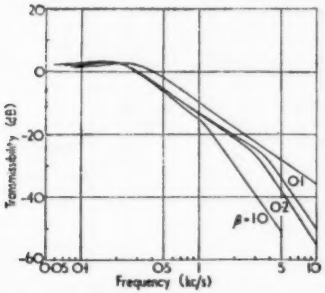


FIG. 15.—The transmissibility of Hycar 1001 in the simple and compound mounting systems. Temperature 17° C. (Experimental points omitted to ensure clarity of figure.)

The transmissibility curves for the compound mounting systems with mass ratios $\beta = 0.1, 0.2, 1.0$ are in good agreement with their theoretical form. The ratios of the secondary and primary resonant frequencies ω_2/ω_1, agree with the values which were calculated (Equation 8) on the assumption that the mount damping was very small. Thus:

	β	0.1	0.2	1.0
ω_2/ω_1	Calculated	6.49	4.71	2.62
	Measured	6.62	4.69	2.66

At frequencies above the secondary resonance, the isolation provided by the compound system becomes rapidly superior to that of the simple system, and Figure 14 indicates the considerable increase in isolation afforded by the former at high frequencies.

The transmissibility of Hycar 1001.—Results of transmissibility measurements on Hycar specimens in the simple and compound mounting systems at 17° C are presented in Figure 15. The mounts are 0.375 in. long and 0.75 in. in diameter.

The primary and secondary resonances of the compound system are heavily suppressed by the high damping possessed by the Hycar rubber. Above the secondary resonant frequency the isolation afforded by Hycar 1001 increases at

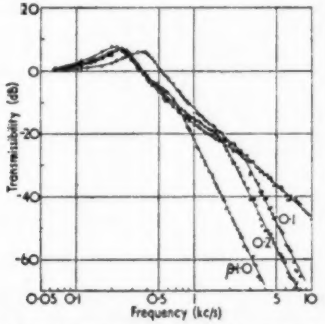


FIG. 16.—The transmissibility of butyl rubber in the simple and compound mounting systems. Temperature 18° C. Mounts contain fifty parts furnace black in one hundred parts butyl rubber.

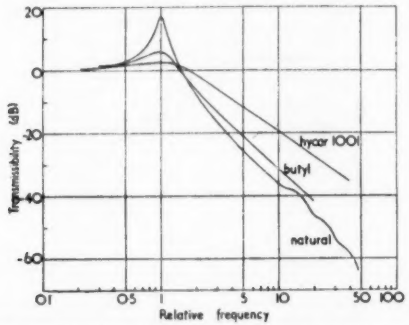


FIG. 17.—The transmissibility of natural, Hycar, and butyl rubbers in the simple mounting system.

16 dB/octave only, as might be expected from consideration of the simple system, where the high frequency isolation increases at 8 dB/octave. In addition, the secondary resonant frequency is displaced towards higher frequencies, namely, the ratio of the secondary and primary resonant frequencies is significantly larger than for natural rubber (Figure 14). The increase in the dynamic modulus of the mounting with frequency is primarily responsible for this behavior.

At frequencies above the primary resonance, the isolation provided by Hycar 1001 in the compound system is never inferior to that of the simple system, but the overall increase in isolation afforded by the compound systems employing small secondary masses is very poor.

The transmissibility of butyl rubber.—The transmissibility of butyl rubber in the simple and compound mounting systems at 18° C is shown in Figure 16. The specimens are 0.5 in. long and 0.875 in. in diameter, and contain fifty parts furnace black in one hundred parts butyl rubber. This proportion of carbon black ensures that a good bond is obtained between the rubber and the metal end pieces of the mounting.

The damping factor of the butyl rubber is equal to 0.58 at a frequency of 360 cps. Although the resonances occurring in the simple and compound

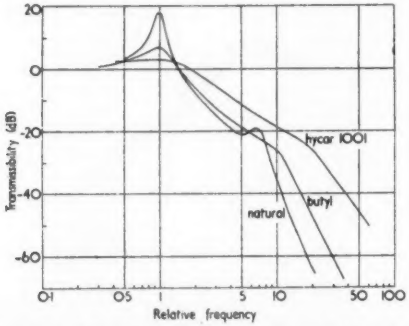


FIG. 18.—The transmissibility of natural, Hycar, and butyl rubbers in the compound mounting system. Mass ratio $\beta = 0.1$.

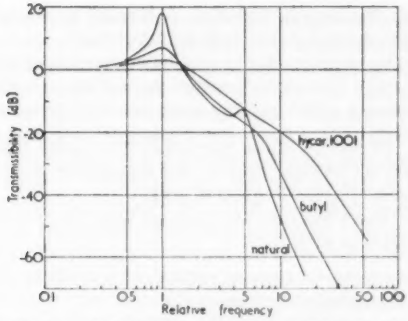


FIG. 19.—The transmissibility of natural, Hycar, and butyl rubbers in the compound mounting system. Mass ratio $\beta = 0.2$.

systems are well suppressed by this high damping, the displacement of the secondary resonance of the compound system towards higher frequencies is appreciably less than when Hycar mounts are employed. The isolation afforded by the simple system above its resonant frequency increases at approximately 10.5 dB/octave, while above the secondary resonance of the compound system, the isolation increases at 22 dB/octave.

Both the relatively small departure made by the rates of high frequency increase in isolation from 12 and 24 dB/octave, and the frequency displacement of the secondary resonance, indicate that the elastic modulus of butyl rubber does not increase greatly with frequency. This is remarkable considering that at the same time the rubber possesses a high damping factor.

CONCLUSIONS

A good anti-vibration mount material should: (i) possess a large damping factor, and (ii) be free from any major increase in dynamic modulus or damping factor with frequency. Thus:

(i) a high mount damping factor provides a low transmissibility at the resonant frequencies of the simple and compound mounting systems,

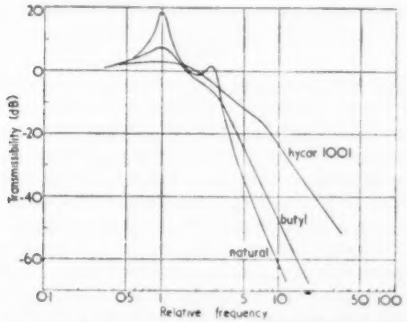


FIG. 20.—The transmissibility of natural, Hycar, and butyl rubbers in the compound mounting system. Mass ratio $\beta = 1.0$.

and reduces the loss in isolation occurring at the resonant modes of vibration possessed by nonrigid foundations;

(ii) if the dynamic modulus of the mount material does not increase greatly with frequency, the anti-vibration mounting provides an isolation at high frequencies which rapidly increases with frequency.

Figures 17, 18, 19 and 20 show previously presented results of transmissibility measurements on natural rubber, the copolymer Hycar 1001, and butyl rubber, redrawn on a relative frequency scale.

It is seen from these figures that natural and butyl rubbers most closely satisfy the above criteria although:

(i) the damping factor of natural rubber is not sufficiently high to suppress resonant transmissibility greatly;

(ii) the dynamic modulus of butyl rubber does increase somewhat with frequency.

The inferior high frequency isolation associated with Hycar 1001 makes its use as a mount material undesirable.

The high frequency isolation provided by castor oil urethane is good, considering the high damping that it possesses, but inferior to that of butyl rubber. Judged by the above criteria, Heveaplus M-G and ordinary polythene are undesirable mount materials because of their relatively low damping. Irradiated polythene in the "rubberlike" state possesses higher damping, but the rate of increase of high frequency isolation is not superior to that of butyl rubber, and the transmissibility at resonance is much greater.

It can be concluded from the results of transmissibility measurements on the above variety of resilient materials that, solely from the aspect of vibration reduction, butyl rubber:

(i) is superior to any of the synthetic materials examined;

(ii) may well compete with natural rubber, because although it exhibits inferior high frequency isolation, this difference:

(*a*) is not excessive and, in fact, is greatest at frequencies where appreciable isolation already exists;

(*b*) may be more than compensated by the lower resonant transmissibility in the simple and compound systems, and the much greater suppression of foundation resonances which butyl rubber affords.

NOTE

The criteria which define a good anti-vibration mount material have been determined solely from the aspect of vibration reduction. No account has been taken of practical problems such as the creep and oil resisting properties of the resilient materials considered above, or of the temperature rise occurring if they are subject to large-amplitude vibration (which in the case of high damping rubbers can cause bond failure after a relatively short mount life).

Rubbers containing a high proportion of carbon black, such as the specimens of natural and butyl rubber employed in the transmissibility measurements above, characteristically possess a modulus that decreases, and a damping factor which increases with the impressed amplitude of vibration[11]. The vibrational amplitudes experienced by the resilient materials in the transmissibility measurements were insufficiently large, however, to invoke such nonlinear properties.

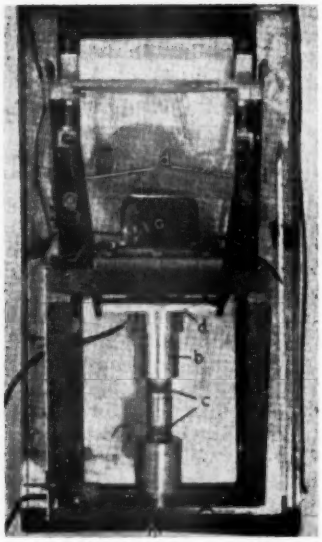
The conclusions drawn from the transmissibility measurements made on the resilient materials considered in this article only apply strictly to the frequency range in which the measurements were made. In practice, the resonant frequency of a vibrating item on its resilient mounting will be the order of one decade lower than in the above measurements. The resonant transmissibility of the resilient materials at the lower frequencies will be somewhat greater than depicted here, as will be the rate of increase in high frequency isolation which they afford. This improvement in isolation will be rather more apparent for the high damping materials, since their elastic modulus decreases more rapidly with frequency than that of low damping materials. It is felt, however, that the conclusions can correctly guide the choice of mount materials for use at frequencies where, in practice, mounting resonances occur. For example, the conclusions drawn from the critical comparison of natural and butyl rubber remain unchanged. Thus, although the suppression of resonant transmissibility afforded by butyl rubber in the simple and compound systems will be less at lower frequencies, it will still be superior to that afforded by natural rubber, but probably by a reduced amount[12]. There is no doubt that at frequencies above the mounting resonances, butyl rubber will continue to offer far greater suppression of foundation resonances than natural rubber.

Reference must also be made to the temperature dependence of the resilient materials considered in this article. The mechanical properties of high damping materials will be the most temperature sensitive. Any temperature variation will be reflected as a change in the suppression of mounting and foundation resonances, and in the high frequency isolation which the materials afford. It is felt that the conclusions will remain valid for all the ambient temperatures commonly met with in practice. For example, in the particular case of a mounting of filled butyl rubber in the simple system, it is thought most unlikely that a change in temperature of plus or minus 10° C from room temperature (20° C) would produce more than plus or minus 2.5 dB change in the resonant transmissibility. Even at higher temperatures it is very probable that the damping of butyl rubber will continue to exceed that of natural rubber. The rate of increase in high frequency isolation which butyl rubber affords will become favorably greater. At lower temperatures, however, the damping factor of butyl rubber will increase, and the high frequency isolation which butyl rubber affords will become less as the temperature decreases. At sub-zero temperatures the high frequency isolation will possibly be much inferior to that of natural rubber. If this is the case, and the mounting is required to operate continually at such temperatures, then natural rubber will definitely prove a more suitable mount material.

APPENDIX

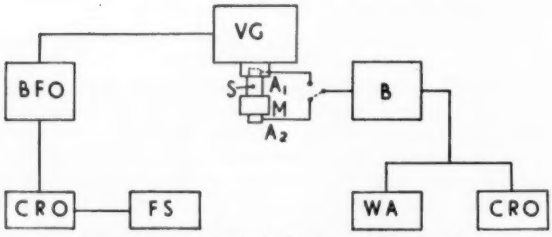
The experimental determination of transmissibility.—Transmissibility measurements have been made on small cylindrical specimens of natural rubber and synthetic rubberlike materials using a method previously employed by Harrison, Sykes, and Martin[5]. These workers have shown from a reciprocity theorem that when the mass M_1 of Figure 21 (*a*) is driven at an angular frequency ω, the ratio of the accelerations A_2/A_1 is identical with the ratio of the forces F_2/F_1 in Figure 21 (*b*). This force ratio is by definition the transmissibility of the simple system with a mount of elastic modulus E, and mass M which vibrates at the angular frequency ω. Transmissibility measurements on resilient specimens in the compound system may equally well be made in this way.

A photograph of the apparatus is shown in Figure 21(*c*). The mass represented by M_1 in Figure 21(*a*) is comprised of a short aluminum beam and aluminum housing, which contains the accelerometer A_1. The elastic modulus represented by E_1 in Figure 21(*a*) is provided by catapult elastic, which softly



(*c*)

a, vibration generator; *b*, accelerometers; *c*, test specimen E in the compound system; *d*, the elements M_1, E_1.



(*d*) F.S., frequency standard; *C.R.O.*, cathode ray oscillograph; B.F.O., beat-frequency oscillator; V.G., vibration generator; *S*, specimen; A_1, A_2, accelerometers; B, amplifier; W.A., wave analyzer.

FIG. 21.—The experimental determination of transmissibility.

suspends the beam and mounting system which is fastened to it. The beam is excited at its midpoint by a small vibration generator, which is driven by a beat-frequency oscillator (Figure 21*d*) at accurately known frequencies in the range 60 cps to 10 kc/s.

The accelerations A_1 and A_2 are measured by barium titanate accelerometers. The amplified accelerometer outputs are compared by a wave analyzer possessing a logarithmic output meter, so that the transmissibility of the test specimen in decibels can be read directly.

The amplitudes of vibration suffered by the resilient materials during transmissibility measurements are very small, and are such that in all cases the materials exhibit linear behavior. For example, with reference to the transmissibility of natural rubber in the simple mounting system (Figure 6), the peak displacement suffered by the rubber at 500 cps is 5.5×10^{-5} cm, and the associated dynamic strain is 4.3×10^{-5}.

SUMMARY

This article attempts to determine, solely from the aspect of vibration reduction, the criteria which define a good antivibration mount material. It concludes firstly that such a material should possess a high damping factor which does not increase greatly with frequency, and secondly, that it should be free from any major increase in dynamic modulus with frequency.

Results of transmissibility measurements on a variety of resilient materials indicate that high damping synthetic rubbers normally possess a dynamic modulus which increases rapidly with frequency. It is shown that this modulus increase is responsible for the poor isolation afforded by these rubbers at frequencies above the resonant frequency of the mounting system, and not their inherent high damping as commonly supposed.

Filled butyl rubber is an exception, affording an isolation at high frequencies not greatly inferior to that of natural rubber, yet at the same time possessing much higher damping.

ACKNOWLEDGMENTS

The author wishes to thank Dr. R. W. B. Stephens and Dr. G. G. Parfitt for their advice and encouragement during the course of this work.

The author also wishes to thank the Andre Rubber Co. for providing specimens of natural rubber, butyl rubber, and Heveaplus M-G, the British Rubber Producers' Research Association for providing the specimen of Hycar 1001; Gestetner Ltd., for providing the specimen of castor oil urethane; and the United Kingdom Atomic Energy Authority for providing the specimens of irradiated polythene.

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CONSTITUTION AND VARIABILITY OF RUBBER FROM INDIVIDUAL TREES *

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Estate crude rubber is the result of blending latex from thousands of trees; therefore, it does not reflect variations in the rubber from individual trees. Rubber produced from young trees is softer than that from older ones and rubber from older trees which are infrequently tapped is likely to be hard and tough. Hard tough varieties of rubber are the up-river, acre and Bolivian fine paras obtained for the most part from very old trees. Other variables in commercial crude rubber in respect to composition, cleanliness, plasticity, curing, and aging properties are well known. Some of these variations are due to variables in collection methods and processing and the source of others has not been determined. Very little detailed study has been made of the rubber direct from individual trees. This situation is largely the result of the lack of suitable methods for such studies and any result of such an investigation probably could not be related to variations in the bulked product.

The purpose of this paper is to present data on the variations in rubber from individual trees. The data were obtained by the use of special procedures, designed to obtain information on several variables under consideration. This type of information is of aid in a better understanding of plant metabolism and synthesis about which little definite knowledge is available. Also in the selection of high yielding trees for bud grafting, added information regarding the nature of the rubber derived from individual trees could lead to the production of a superior type of estate rubber.

The exact nature and variations in the soluble and difficultly soluble fractions in latex and crude rubber are still not fully understood and the information in this paper is directed towards presenting more definite knowledge along this line.

In 1951, Bloomfield[2] published a series of papers, giving results of a study of Malaya estate rubber from a few freshly tapped individual trees. The results of the present investigation will be closely compared with those of Bloomfield. His investigation was directed mainly to variations in solubility, viscosity and molecular weight distribution of the sol hydrocarbon portion in the rubber from individual trees.

PREVIOUS DATA AND TECHNIQUE

In order to compare the results on rubber direct from different trees with those from samples of crude rubber of commerce, Table I includes some data previously published by the writer[3], but presented here in a different manner. These data give the amount of sol and its intrinsic viscosity in various samples of crude rubber with different solvents. The standard procedure used in the older study and in the present work is to place 0.1 g of a finely cut sample in

* Reprinted from *Rubber Age*, Vol. 85, 773-782 (1959).

100 ml of solvent. A screw cap bottle is employed which is immediately placed in a dark cabinet for six to seven days. Following this period the swollen difficulty soluble gel is usually found intact and an aliquot of the clear solution can be pipetted out and its viscosity determined in a suitable viscometer at 20.0 or 25.0° C followed by measuring the viscosity on less concentrated solutions of the same sol to obtain intrinsic viscosity data. In the case of the more soluble samples, a loose flaky gel is found and filtration must be resorted to. In this case, the solution is filtered through a very open filter paper in a closed system to avoid loss of solvent. An aliquot is removed to determine the amount of rubber in solution by removal of the solvent in an evaporating dish which is warmed while a stream of carbon dioxide is passed over it.

TABLE I

SOLUBILITY AND VISCOSITY OF RUBBER IN VARIOUS SOLVENTS [a]

Rubber type	Solvent used	Solubility, %	Intrinsic viscosity
No. 1 smoked sheets	Chloroform	85.0	6.39
	Benzene	81.5	6.81
	Carbon tetrachloride	79.0	6.81
	Cyclohexane	67.7	7.50
RCMA crepe	Chloroform	86.0	6.51
Thick crepe[b]	Chloroform	85.0	6.45
	Benzene	74.7	6.65
	Chlorobenzene	83.5	6.72
Bolivian fine para	Chloroform	61.6	7.84
	Benzene	51.0	7.62
Commercial latex film	Chloroform	62.3	7.00
	Hexane	6.4	1.42
Commercial latex film, washed	Chloroform	66.6	8.46
	Hexane	9.7	3.13
Com. latex, acid coagulated	Chloroform	56.8	8.10
	Hexane	5.6	1.70

[a] Data, except (b) taken from article by Kemp and Peters, all samples air dried. *Ind. Eng. Chem.* 33, 1391 (9141); RUBBER CHEM. & TECHNOL. 15, 1 (1942).
[b] Crepe after keeping 8 years in dark at room temperature.

The results in Table I show that smoked sheets and crepe give about the same results in benzene and chloroform which the writer considers to be the most suitable solvents for this work. Crepe has a higher purity, but is milled more during washing. These are offsetting factors affecting solubility and viscosity. Samples of rubber under test should not be exhaustively dried when benzene is used for this work since it has been shown[3] that this results in a large decrease in solubility and viscosity. Chloroform is a somewhat faster acting solvent than benzene. It contains a small quantity of alcohol for stabilization and drying the rubber does not affect the results obtained with it. For this reason chloroform is preferred over benzene.

RUBBER FROM FLORIDA

From the period 1939 to 1943 the writer conducted studies on rubber from the various species of trees and plants at the U. S. Department of Agriculture Plant Introduction Garden at Chapman Field, Miami, Florida. The rubber trees there were raised from seed and were about 10 years of age[4]. The growth

of these trees was slow and their yield of latex low, reflecting the unsuitable climatic conditions for rubber culture. However, the larger and older of these trees were healthy and yielded latex which appeared fairly close to normal. The results obtained in this study were not published because it was felt they might not truly reflect those that would be obtained from healthy trees in the producing areas and therefore be misleading.

Method of collection.—In connection with the study in Florida a satisfactory method was developed for sampling and preserving rubber taken directly from the tree which permits many variables to be studied. It consists in allowing a few ml of the latex from a fresh tapping cut to flow into about 50 ml of either 95 per cent or absolute ethyl alcohol. This procedure results in immediate and complete coagulation of the rubber and kills all bacteria present in the latex. One can also note the color and hardness of the coagulum, the nature of the serum and amount of nonrubber constituents separating from the serum on standing. The rubber which is immersed in the alcoholic serum is very stable

TABLE II

SOLUBILITY AND SOL VISCOSITY IN CHLOROFORM OF FLORIDA RUBBER[a]

Rubber species	Solubility, %	Intrinsic viscosity
Hevea tree 1533	100	5.04
Hevea tree 517 (1st tap)	100	5.84
Hevea tree 517 (2nd tap)	100	5.82
Hevea tree 514	100	5.61
Manihot Glaziovii	88	3.13
Funtumia	100	7.47
Cryptostegia hybrid	100	6.90
Hevea tree 1533, latex dried in vacuum	100	4.90
Hevea tree 514, latex dried in vacuum	100	6.23

[a] Alcohol coagulum pressed free of serum, finely cut and air dried in dark.

and conditions are ideal to resist aging and any changes in any of the constituents. Some of the proteins will precipitate from the serum. The samples are best preserved over long periods in an ice box at about 40° F and under this condition changes are practically nil over long periods of a year or more.

In Table II, data are presented on rubber samples collected as described above from different species of trees as well as from cryptostegia hybrid. It is seen that with the exception of the Manihot sample, all rubbers from Florida were completely soluble. The hevea samples were somewhat soft compared with No. 1 crepe and this is reflected in their lower viscosities and freedom from any insoluble fraction. Funtumia, a hard tough rubber, is recognized as a high grade type and it differs mainly from hevea in its somewhat higher content of resins. It does not respond to acid coagulation but alcohol coagulates it immediately. The high viscosity of its sol is evidence of the high average molecular weight of its hydrocarbon compared with hevea grown under the same adverse Florida climate for rubber culture.

Cryptostegia hybrid rubber is grown in Florida under favorable conditions and is completely soluble with high intrinsic viscosity[1] equal to the best grades of estate rubber. Johnson[5] found a sample of this type of rubber to be only partly soluble in toluene which may have been due to some aging effect after collecting.

RUBBER DIRECT FROM TREES IN COSTA RICA

Through the courtesy of the Goodyear Tire & Rubber Company, the writer was permitted to visit their Speedway Estate located at LaFrancia on the eastern slope of Costa Rica about 90 miles southeast of San Jose. The trees in this 1500 acre estate were planted from seedlings about 16 years ago. The annual rainfall in the area averages about 150 inches and cloudy weather is more frequent than in the better rubber producing areas. This has led to some infection of the dreaded leaf fungus disease. All trees were being regularly tapped and the tapping system used was full spiral every four days.

TABLE III

SOLUBILITY AND SOL VISCOSITY OF RUBBER[a] FROM INDIVIDUAL TREES IN COSTA RICA

Tree no.	Color	Solubility, %		Intrinsic viscosity		Firmness
		Chloroform	Benzene	Chloroform	Benzene	
1	Light cream	80	80	5.87	5.77	Normal
2	Cream	90	86	6.65	6.52	Normal
3	Light cream	67	67	7.01	6.83	Hard
4	Light cream	61	60	6.71	6.51	Hard
5	Light cream	96	94	5.40	5.06	Soft
6	Light cream	89	—	6.35	—	Normal
7	Light cream	65	—	8.21	—	Hard
8	Light cream	80	—	7.36	—	Normal
9	Grey, mottled	81	—	7.29	—	Normal
10	Light cream	65	67	6.51	5.86	Hard
11	Cream	77	76	8.44	8.14	Hard
12	Light cream	84	—	5.63	—	Soft
13	Light cream	81	—	5.75	—	Soft
14	White	62	—	7.37	—	Hard
15	Grey, mottled	92	—	5.52	—	Soft
16	White	84	—	5.45	—	Soft
17	Yellow	67	—	7.36	—	Hard
18	Light cream	76	—	7.02	—	Hard
19	Light cream	90	—	6.03	—	Normal
20	Light cream	95	—	5.80	—	Soft
21	Cream	98	—	5.93	—	Soft
22	Grey, mottled	92	—	5.98	—	Soft
23	Grey, mottled	86	—	5.14	—	Soft
24	White	95	—	6.88	—	Normal long fibered

[a] Alcohol coagulum pressed, finely cut and air dried in dark.

An area was selected for taking samples where the trees were uniform and quite normal and healthy and 24 trees located adjacent to one another were tapped into separate containers containing alcohol. These trees bunched close together were selected in order to study differences between individual trees rather than other factors. The trees were tapped and in a few minutes, when the latex was running freely into the cup, a few ml were allowed to drip directly into the alcohol which brought instant coagulation. When one or two grams of rubber were collected from each tree, the writer proceeded immediately to the next tree requiring less than one hour to collect all 24 samples. A bulk sample from 10 trees nearby was collected after flow had stopped and this rubber was immediately coagulated by adding an excess of alcohol. A sample of the bulked estate latex collected for the day was taken before dilution and addition of sulfite and this latex was also coagulated with alcohol. Also a

sample of acid coagulum from the bulked estate latex of the same day's production was soaked in alcohol and squeezed as free as possible of serum. A sample of regular production crepe was taken from the dryer for comparison and this appeared to be high grade and normal in every respect.

Table III presents the data on the latex from individual trees and Table V on the bulked samples compared with crepe. It is seen from Table III that very large differences occur in rubber from different trees. As far as the author is aware, mottled grey rubber has not previously been reported. This grey color was not evident in the latex samples from trees 9, 15, 22 and 23 which appeared normal on tapping. The grey mottled appearance results from the presence of clotted lutoids in the latex[6]. The color of the rubber between the grey blotches was a normal cream color. Rubber from trees 14, 16 and 24 was practically white, while aside from the grey samples, the remainder ranged from light to deep cream or yellow color. The solubilities in chloroform showed a wide range from 61 to 98 per cent while the intrinsic viscosities[1] range from 5.14 to 8.44. In cases where the solubility was high and the viscosity low, the rubber was soft.

TABLE IV

EFFECT OF EXHAUSTIVE DRYING[a] ON SOLUBILITY AND VISCOSITY OF SAMPLE NO. 17 IN VARIOUS SOLVENTS

Solvent	Solubility	Intrinsic viscosity
Chloroform	66	7.40
Chloroform[b]	67	7.81
Benzene	57	6.44
Benzene[c]	45	6.90
Toluene	54	6.81
m-Xylene	68	5.15
Carbon tetrachloride	26	4.96
Chlorobenzene	62	4.90
Cyclohexane	21	3.98

[a] Alcohol coagulum from tree 17 pressed, finely cut and dried in vacuum desiccator one week (0.1 g in 100 ml solvent for 7 days).
[b] In solvent 10 days.
[c] Sample dried 5 weeks in desiccator.

It was previously shown[3] that exhaustive drying of crude rubber greatly reduces its solubility in benzene but has practically no effect on solubility in chloroform which the writer finds to be the best and most powerful solvent for rubber. This fact cannot be stressed too highly as benzene has been the most widely used solvent in research work on rubber. This effect is apparently connected with the gel or difficultly soluble portion and those samples of rubber having the highest gel content are the ones which show the greatest effect of drying on their solubility in benzene.

In order to show the effect of drying on the solubility in various solvents a sample of caogulum from tree No. 17 was dried exhaustively for one week. The results given in Table IV show this effect in striking fashion.

When crude rubber is dried in air at ordinary temperatures it shows about the same solubility in benzene, toluene and chlorobenzene and a somewhat lower solubility in cyclohexane and carbon tetrachloride as compared to chloroform[3]. It is seen in Table IV that chloroform is the only solvent in which the solubility of rubber with a high gel content is unaffected by exhaustive drying.

Rubber deteriorates rapidly in chlorobenzene and carbon tetrachloride

especially when exposed to light for very short periods; therefore, these solvents should be avoided.

It was found during the work in Florida that rubber latex when spread thinly on a glass plate and dried quickly under a vacuum desiccator will redisperse almost completely when placed in water. When the film is heated an hour at 50° C, it slowly sets up, but when the temperature is raised to 80° C it no longer disperses. In a similar manner, the freshly tapped and dried film will disperse almost completely when immersed in petroleum ether and shaken but after heating at 80° C then only about 40 per cent dissolves and the difficultly soluble portion is swollen into a coherent gel.

Bloomfield[2] tapped about one ml of the latex directly into 100 ml of benzene and after shaking, the dispersion was complete. After removing the water under reduced pressure at 30° to 35° C, the solution was filtered and its viscosity and concentration was then measured and reported as latex solution viscosity or LSV values. These LSV values expressed as intrinsic viscosity[1] ranged from 4.80 to 7.20 for seven trees with the average equal to 5.80.

TABLE V

COMPARISON OF SOLUBILITY AND VISCOSITY IN CHLOROFORM OF INDIVIDUAL TREE SAMPLES WITH BULKED SAMPLES AND CREPE

Description of sample	Solubility, %	Intrinsic viscosity
Range of 24 individual trees	61–98	5.14–8.44
Average of 24 individual trees	80	6.42
Costa Rica regular crepe	86	6.46
RCMA crepe	86	6.51
Thick crepe	85	6.45
Bulked alcohol coagulated latex from 10 trees, no ammonia added	80	6.95
Regular alcohol coagulated Costa Rica bulked field latex on arrival	76	6.95
Regular factory diluted and acid coagulated Costa Rica field latex[a]	78	7.36

[a] Considerable maturation occurred during 2 weeks before sample was tested.

Another of Bloomfield's procedures was to add to the dry latex solution in benzene an equal volume of a mixture of 70–30 methyl alcohol-benzene. This precipitates most of the rubber hydrocarbon in a fairly pure form removing a considerable part of the nonrubber constituents. This partially purified rubber was then placed in benzene and in this case of latex from two trees there remained 20 per cent insoluble gel in one and 41 per cent in another. The sol components of each had a higher intrinsic viscosity than the whole rubber in benzene. In the case of rubber from the same seven individual trees mentioned above the sol viscosities of the purified rubber ranged from 6.50 to 9.18 with the average being 7.58 which is about 30 per cent higher than for the whole rubber in the LSV measurements for the same trees.

It must be pointed out that the difficultly soluble fraction present in the whole rubber contributes very little to viscosity since very little of it is dispersed as is the sol fraction. The insoluble fraction probably is present in the benzene as highly swollen finely dispersed gel particles and as such contribute little to the viscosity as was pointed out recently by Freeman[7]. In addition, the soluble nonrubber constituents present in the LSV measurements reduce the viscosity practically in proportion to their content which Bloomfield esti-

mates at about 10 per cent. If we take the average insoluble fraction content of 20 per cent found by the writer in Costa Rica latex and add the 10 per cent nonrubbers the increase of the viscosity of the sol in the purified rubber of 30 per cent over the LSV values can be fully accounted for.

It is seen in Table V that the range of sol intrinsic viscosity for the alcohol coagulated rubber from latex taken from 24 different trees is 5.14 to 8.44 and these results are close to those found by Bloomfield for purified rubber. The alcohol coagulated product still contains a substantial portion of the nonrubbers which accounts for their being on the average about 15 per cent lower. Some of the lowest molecular weight hydrocarbons may also have been removed by

TABLE VI

FRACTIONATION OF COMPOSITE FROM TREES 1–5

Fraction no.	Solvent, benzene-alcohol	Time, days	Extract, %	Intrinsic viscosity, Chloroform	Nature of Extract
1	200 ml 40–60	2	2.00	—	Resin
2	200 ml 50–50	2	0.33	—	Resin
3	220 ml 59–41	3	0.70	0.10	Soft, sticky, yellow
4	233 ml 70–30	4	0.96	0.55	Soft, sticky, pasty yellow
5	100 ml 72–28	3	0.53	0.47	Same as for Extr. No. 4
6	100 ml 77.5–22.5	3	2.01	0.55	Firm, pasty, slightly elastic
7	100 ml 77.5–22.5	4	4.00	1.08[a]	Soft rubber, slightly elastic
8	100 ml 80–20	2	6.60	1.89[b]	Soft rubber, slightly elastic
9	425 ml benzene	7	57.00	9.90	Tough, elastic, colorless
10	———	7	25.87	—	Residual gel
			100.00		

[a] (η) in Skellysolve B 0.65—*n*-Heptane 0.63.
[b] (η) in Toluene 1.77—in cyclohexane 1.87

Bloomfield's purification method. On the whole, the agreement between the two investigations is very good. The larger number of trees studied by the writer must also be considered in the comparisons made above, although even in the case of 24 trees, this is only a very small sampling to obtain an insight into the full spread of the variables involved in rubber produced by individual trees. It is truly remarkable that such wide differences were found in the case of only 24 trees of the same age growing adjacent to one another and tapped at the same time. This illustrates that the method of alcohol coagulation is one which is well suited for such a study. A much broader study using this method should yield very valuable information for rubber producers since some individual trees produce superior rubber in respect to color, texture, solubility and viscosity. A broad study of these and other factors together with yield should

enable one to select the superior trees which could be used in bud grafting to build up an estate which would produce a higher quality and more uniform product.

Van Essen[8] published results on the vistex viscosity resulting from tapping 34 individual trees in Indonesia into a mixture of 70 volumes of toluene and 30 of pyridine. Values ranging from 3.52 to 7.10 with an average of 5.0 were obtained. Such vistex values are considerably lower than obtained on the same latex rubber in chloroform but these results do show the wide variations in rubber from different trees. That individual rubber trees show these differences probably is related to their heredity. The original seeds brought out of South America no doubt produced trees which differed in certain respects and

TABLE VII

FRACTIONATION OF COMPOSITE FROM RUBBER[a] TREES 7, 14 AND 17

Fraction no.	Benzene-alcohol	Time, days	Extract, %	Intrinsic viscosity in chloroform	Nature of extract
1	75–25	5	1.94	—	
1A	—	—	1.00	—	Resin extract from 1 with acetone
1B	—	—	0.94	0.56	Residual rubber in 1
2	75–25	6	0.90	0.79	Yellow, soft, sticky plastic
3	78–22	7	5.2	0.83	Light, yellow, soft plastic
4	80–20	4	7.0	2.18[b]	Pale yellow, some elasticity
5	80–20	7	2.6	2.42[c]	Pale yellow, some elasticity
6	82–18	7	15.2	7.59[d]	Nearly colorless, hard, tough, elastic
7	82–18	7	20.8	9.31[e]	Colorless, hard, tough, elastic
8	82–18	8	12.5	8.05[f]	Yellow, tough, elastic
9	82–18	11	6.5	7.88	Yellow, tough, elastic
10	Gel residue	—	25.42	—	

[a] 2.5 g of alcohol coagulum pressed, finely cut and dried in air, in dark.
[b] Fraction 4 in C_6H_6 (η) =2.01.
[c] Fraction 5 in C_6H_6 (η) =2.32.
[d] Fraction 6 in C_6H_6 (η) =7.29. Toluene 6.90—Cyclohexane 8.31.
[e] Fraction 7 in C_6H_6 (η) =9.02.
[f] Fraction 8 in C_6H_6 (η) =7.98.

may even have involved a mixture of species. It is known that no two rubber seeds from different rubber trees have the same marking, which is evidence that each tree is an individual. Using the methods of the present study, it would be of interest to extend the investigation making a more extensive study of different species of hevea in their native locations along with many other important variables.

Bloomfield[3] found that rubber from older trees which had not been tapped for 8 to 20 years was much harder and less soluble in benzene than rubber from regular tapping. He estimated the socalled gel content in this rubber by determining the amount of rubber remaining undissolved in a mixture of 80 volumes of benzene and 20 volumes of methyl alcohol after three days at 30° C. This undissolved portion ranged from 85 per cent at the first tapping and

dropped to 66 per cent at the 25th tapping. Data were presented on the so-called gel content of the six trees reported on and these ranged from 51 to 88 percent. It should be pointed out that a large proportion of this socalled gel fraction is soluble in benzene or chloroform since only the lower molecular weight portion of the rubber is soluble in an 80–20 mixture of benzene and methyl alcohol as will be shown later in Tables VI, VII and VIII. This method of test is therefore not a good procedure to show the differences between old untapped trees and regularly tapped ones. There is, however, other good evidence to indicate that the older trees do produce a harder rubber. This variable should be explored further by using the methods used in the present investigation.

TABLE VIII

FRACTIONATION OF COSTA RICA CREPE
(2.5 g in 100 ml solvent)

Fraction no.	Solvent, benzene-alcohol	Time, days	Extract[a], %	Intrinsic viscosity
1A	75–25	7	2.34	Resin
1B	75–25	7	1.53	0.64
2	75–25	6	1.28	0.64
3	78–22	13	3.90	0.99
4	80–20	9	9.18	1.60
5	80–20	36	5.12	1.77
6	81–19	7	12.65	4.35
7	Benzene	11	12.87	7.05
8	Benzene	10	31.45	6.85
9	Benzene	7	3.27	6.90
Gel residue	—	—	16.41	—
			100.00	

[a] Table VI—16.1% int. vis. range 0.1–1.89.
Table VII—18.4% int. vs. range 0.56–2.42.
Table VIII—23.3% int. vis. range 0.64–1.77.

An investigation of the solubility of fresh latex in petroleum ether was carried out by Verbrugh[9] in Java in 1941 and he found that when the latex was collected and dried without exposure to air or light, the maximum amount of rubber soluble in petroleum ether was 66 per cent. The swollen gel however was loose and flaky and would disperse on gentle agitation. These results confirm the present ones obtained in Florida. The maximum solubility found by the writer[10] for acetone extracted Java crepe in mixed hexanes (Skellysolve B) after exhaustive treatment for long periods with several solvent changes was 53 per cent. The higher value found by Verbrugh was probably due to the presence of resins and other petroleum ether soluble nonrubber constituents not present in crepe rubber.

Bloomfield[3] determined the insoluble fraction, which he termed microgel, by petroleum ether extraction of thin films of latex dried in nitrogen, the latex being taken from seven individual trees. The soluble fractions ranged from 33 to 79 per cent, the average being 55 per cent. The value for normal bulked latex was 52 per cent.

In view of these data it is seen that the sol fraction in fresh latex rubber is about the same as in crepe, but the insoluble swollen gel is of a loose structure which can be more readily dispersed. Upon drying or heating and standing as in the manufacture of crepe and smoked sheet, the difficultly soluble or gel fraction present in the orignial latex is much firmer and swells less in solvents.

It must be noted that the insoluble residue or gel from petroleum ether or hexane extraction is larger in quantity and not to be confused with the residual undissolved gel from benzene or chloroform extraction, since hexane or petroleum ether will not dissolve the higher molecular weight fractions due to their limited solubility in these solvents. In crepe rubber about 50 per cent is soluble in hexane while for the same rubber 80 to 85 per cent is soluble in chloroform or benzene.

In the case of a sample of alcohol coagulated Costa Rica latex solubility in benzene was 81.0 per cent and intrinsic viscosity of the sol was 6.74. In hexane under the same conditions the solubility was 40.5 per cent and intrinsic viscosity 4.88. This shows that hexane, which is similar to petroleum ether in solvent power, fails to dissolve the higher molecular weight fraction in rubber. The undissolved residue from petroleum ether or hexane is a highly swollen gel but it is quite different from the residue from chloroform or benzene extraction.

FRACTIONATION OF FRESH LATEX RUBBER

Crude rubber has been proven to consist of a series of soluble polymer fractions varying quite broadly in molecular weight and a gel which is difficultly soluble in solvents such as benzene or chloroform, varying in quantity usually in the range of 10 to 25 per cent for crepe or smoked sheet up to about 35 per cent in the case of latex and wild rubber. These values are based on using benzene or chloroform and 0.1 g of finely cut rubber in 100 ml of solvent and standing in the dark for 6 to 10 days to allow the sol fraction to dissolve without shaking.

A previous fractionation[10] of acetone extracted crepe rubber used 5 g of finely cut rubber in 250 ml of mixed hexanes (Skellysolve B). The solution was decanted from the swollen gel eleven separate times and replaced with fresh solvent and the periods of each treatment varied from one hour to 48 days. The first 1 hour fraction dissolved was 4.4 per cent with an intrinsic viscosity of 2.66 and each fraction showed an increase in viscosity up to the 9th fraction was reached and 46 per cent of the sol had been extracted. At this point, the solubility of the residual rubber reached a constancy of 0.1 per cent and the intrinsic viscosity of the remaining four fractions remained practically constant ranging from 7.13 to 7.54. Although the last fractions were very narrow in molecular weight distribution, the first ones were not, since their solubility in hexane is high, a wide range of molecular weights would be expected. This work pointed up the fact that the higher molecular weight fractions do have a very limited solubility and require long periods to saturate the solvent by diffusion.

Bloomfield[2] carried out fractionation of rubber latex from different trees tapped directly into benzene in Malaya by adding 30 per cent methyl alcohol to the warm mixture until incipient precipitation started and then cooling in various stages. Insoluble fractions in benzene of 14 to 23 per cent first precipitated and several other fractions totaling 70 to 80 per cent were thrown out of the solution at reduced temperatures and had inherent viscosities[1] of 1.3 to 11.5 in alcohol free benzene.

In order to study the full scale of molecular sizes in rubber direct from the tree, two separate fractionations were carried out. In one fractionation, a composite of alcohol coagulated samples number 1 to 5 inclusive and in the other, the rubber involved a mixture of samples number 7, 14 and 17. The first series were more or less normal with average viscosity while 7, 14 and 17

were all hard with high sol viscosity and high contents of the difficultly soluble fraction ordinarily called gel.

The samples were finely cut and 1.5 g in the case of the 1–5 blend were placed in benzene methyl alcohol mixtures in a dark cabinet starting with low benzene ratios and increasing with different fractions. Each fraction was the result of extraction by diffusion after several days standing in the dark. The amount extracted was determined by decanting the solution from the gel, evaporating a measured volume of solution, evaporating to dryness in a stream of CO_2, and weighing the residue. The viscosity of the fraction was determined when dissolved in benzene or chloroform. The viscosities of some fractions were determined in several solvents for comparison. In the case of 1-5 blend after the lower fractions were removed, the remaining rubber was treated with 425 ml of benzene and a large fraction removed leaving the swollen gel residue.

In the case of blend 7, 14 and 17, a somewhat different procedure was followed, using 2.5 g in 100 ml of solvent sample and carrying out a more detailed and exhaustive fractionation. Carbon dioxide was kept over the solvents at all times and the flasks kept in a dark cabinet at room temperature 20° to 30° C.

The results in Tables VI and VII show the wide distribution of molecular sizes of the rubber fractions which can be shown to be present in rubber direct from the tree. The lower members are more clearly separated by the diffusion procedure than was the case in Bloomfield's[2] investigation using precipitation which placed emphasis on the higher members. Dropping the alcohol concentration from 80–20 to 82–18; a critical point is passed at which the solvent mixture becomes an excellent solvent for the higher members.

About 8 per cent of the rubber has an intrinsic viscosity ranging up to 1.0 and about 7 per cent from values of 1.0 to 2.0. From this point the fractions showed a rapid rise in viscosity to a maximum of 9.9.

In order to compare the regular Costa Rica crepe rubber with the product coagulated with alcohol from the latex of individual trees, a fractionation was made of the regular crepe which was a result of mixing the latex from about 50,000 trees in the bulking tank used for daily production. These data are given in Table VIII and it is seen that the Costa Rica crepe has slightly higher amounts of the lower fractions, and a higher sol content as compared with that shown for the rubber taken direct from the tree shown in Tables VI and VII. The average sol content of the rubber from 24 trees was 80 per cent, whereas regular Costa Rica crepe was 86 per cent. The average intrinsic viscosity of the rubber from the 24 trees was 6.42 and the crepe in chloroform as shown in Table V was 6.46.

It can be concluded from this study that the preparation of crepe, which involves considerable mill washing, increases the amount of sol and decreases the gel content a few per cent, but does not appreciably affect the viscosity of the sol fraction.

NATURE OF DIFFICULTLY SOLUBLE GEL FRACTION

The blend of samples 1 to 5 shown in Table III had an average gel content of 21 per cent whereas the gel residue from fractionation of this blend was 25.87 per cent as seen in Table VI. This higher gel content from fractionation is due to a less exhaustive extraction of sol than was the case in the blend of samples 7, 14 and 17 which showed after fractionation a residual gel content 9.3 per cent less than the average given for these samples in Table III.

Freeman[7] showed that the gel was present in latex as separate ultrafine

particles which pass through a No. 1 sintered filter when fresh latex is dispersed into benzene or a vistex solution. These gel particles could be separated by adsorption on powders or by high speed centrifuging the vistex solutions. It is therefore reasoned that in coagulated latex rubber the gel is dispersed in the sol as minute particles. This gel phase can be dispersed into smooth solvent cements or ballmilling with the addition of a little butyl alcohol. Upon solution by diffusion into a good solvent without agitation the sol is extracted and the gel particles remain and become coalesced and highly swollen.

The physical nature of the gel gives strong evidence that it is the product of linking of isoprene chains either by oxygen or carbon-to-carbon links.

The gel from the fractionation shown in Table VII was covered with methyl alcohol and pressed into a smooth compact sheet. It was then dried in a stream of CO_2. Measurements showed it had an elongation of about 300 per cent and a tensile strength of about 150 kg/cm^2 (2100 psi).

The swelling index in chloroform of the gel was 24 and 16 in benzene whereas a vulcanized rubber band showed a swelling index of 7.

This gel will not dissolve in boiling tetrachlorethane which is a good solvent for soft vulcanized rubber. This might indicate a carbon-to-carbon linkage is involved instead of oxygen as is generally believed.

On account of the difficulties of purifying gel residues from solvent extraction from proteins, lutoids and other substances, no direct evidence of oxygen content is available, however, the method of separation by centrifuge as practiced by Freeman[7] might provide a suitable sample for analysis.

It was found[3] that chloroform residual gel after passing several times hrough a tight mill would dissolve and that filtration then removed most of the protein and other impurities. The iodine value from this broken down gel was found to be 355. This corresponds to 95 per cent of the theoretical unsaturation of polyisoprene and is close to the value found for acetone extracted crepe rubber[11]. Analysis of the original gel showed a nitrogen content of 2.25 per cent and 1.32 per cent ash whereas the broken down sol derived from this gel contained 86.97 per cent carbon, 11.70 per cent hydrogen and 0.21 per cent nitrogen with a hydrogen-carbon ratio 1.602 or very close to theory. The gel stretched 120 per cent gave the polyisoprene x-ray diffraction pattern.

The fact that different trees produce widely different amounts of gel is undoubtedly connected with differences in their synthesis. The mechanism whereby this takes place is not known because little positive information on the chemistry of rubber synthesis in the plant is available.

SOLUBILITY AND VISCOSITY OF GEL

After exahustive extraction of the gel of Table VII it was of interest to determine solubility in different solvents and the viscosity of the solutions obtained since these data might throw some light on structure.

Accordingly after drying, 0.1 g of this gel was finely cut and placed in 50 ml of solvent in the dark with the air having been displaced over the solvent with CO_2. After several days the solution was decanted from the swollen gel and sol content and viscosity determined. This procedure was repeated several times and the results obtained are shown in Table IX.

It is seen that the average solubility in benzene or chloroform is about 0.01 per cent and intrinsic viscosity 2.6. The solution may not have been completely saturated in every case. After eight treatments with chloroform, forty per cent of the gel had been dissolved and the results indicate that this gel is a

fairly uniform substance which is the result of some crosslinking reaction in the plant synthesis of rubber.

CONSTITUTION OF SOL RUBBER

Bloomfield and Farmer[12] found the most soluble and the lowest viscosity fractions from crepe rubber contained up to 3.5 per cent oxygen and that the oxygen content decreased steadily as the fractions increased in viscosity.

Midgley and coworkers[13] found 0.04 per cent oxygen in purified crepe whole sol, half of which they found combined as hydroxyl.

TABLE IX

FRACTIONATION OF GEL

(0.1 g of gel in 50 ml solvent)

Fraction no.	Extraction time, days	Solubility of gel, g/100 ml	% gel dissolved in 50 ml	Intrinsic viscosity of solution[a]
		In chloroform		
1	6	0.0100	5.0	3.27
2	4	0.0102	5.2	1.70
3	6	0.0132	6.6	3.28
4	8	0.0136	6.8	1.84
5	7	0.0062	3.1	2.13
6	6	0.0072	3.6	2.62
7	7	0.0110	5.5	2.06
8	19	0.0080	4.0	4.10
	average	0.0099	5.0	2.63
		In benzene		
1	10	0.0124	6.2	2.23
2	6	0.0080	4.0	1.81
3	7	0.0072	3.6	2.40
4	19	0.0100	5.0	2.76
5	14	0.0064	3.2	3.61
	average	0.0088	4.4	2.56

[a] Relative viscosities of solutions of 25.0° C ranged from 1.0151 to 1.0452.

Bloomfield[2] showed that rubber taken fresh from the tree contained oxygen in the lower fractions as was previously found in crepe rubber. About half of this oxygen was combined with active hydrogen and may therefore be combined as hydroxyl.

The present investigation also has shown the presence of these yellow, soft, sticky, low viscosity fractions in rubber taken directly from the trees in Costa Rica. The present author[3] also found 2.3 per cent of crepe rubber was present in fractions ranging in intrinsic viscosity from 0.4 to 1.4. The iodine value of these fractions ranged from 359 to 363 which is close to the value of polyisoprene of 373. Some of the double bonds are apparently saturated with oxygen.

Altman[14] has pointed out that due to the presence of powerful peroxidases rubber may be oxidized and broken down in the tree and this might explain the presence of the low fractions containing oxygen. On the other hand, the plant synthesis of rubber may involve precursors which contain oxygen and these may remain combined at the chain terminals. The presence of powerful antioxidants in the latex would act to limit oxidation after the polyisoprene is formed.

Although the greater part of natural rubber direct from the tree contains high molecular weight straight chain polyisoprene sol with a *cis* head-to-tail structure, it may contain a very small amount of combined oxygen. In addition, rubber contains a few per cent of soft, sticky, low viscosity polyisoprene containing a substantial amount of combined oxygen, together with varying amounts of a difficultly soluble gel. This gel appears to have a three dimensional structure of polyisoprene from such evidence that is available. The present study also indicates the presence of a nonlinear polyisoprene in the sol fraction.

MOLECULAR WEIGHT OF RUBBER

Widely divergent results have been reported for the average molecular weight of sol rubber in crepe, smoked sheets and in the average rubber latex fresh from the tree. The intrinsic viscosity range in benzene or chloroform for the whole sol in these types of rubber is quite narrow in most cases, the average being about 6.5 and rising to about 6.6 with the resins removed. It is, therefore, obvious that the extreme values given in the literature for the molecular weight of sol rubber must be the result of differences in the methods and procedures employed.

Caspari[15] was the first in 1914 to estimate the number average molecular weight of acetone extracted crepe sol in benzene and light petroleum solvents using the osmotic method. His data led to an estimate of about 125,000 for the molecular weight of whole crepe or about 100,000 if a correction in the concentration of the solutions was made for the usual gel content found in crepe rubber, which would not contribute appreciably to the osmotic pressure. Caspari's work was very carefully carried out using a porous cup impregnated with sulfur chloride vulcanized rubber as the semipermeable membrane and allowing long periods to reach equilibrium.

The estimates of numerous other investigations following Caspari up to the present time using osmotic, viscosity, ultracentrifuge, light scattering and chemical means range from 68,000 to about 1,500,000. The more recent publications appear to be accepting the higher values which are based on the osmotic method.

The osomotic method if not subject to variations due to procedure should yield absolute values; however, it has been recently recognized that membrane and other difficulties in the osmotic method lead to abnormally high results which are many fold higher than the true values.

Staudinger's viscosity method indicated the molecular weight of crepe rubber sol to be about 150,000, a value close to that found by Caspari.

Until more work has been carried out to standardize and prove the osmotic method the writer is of the opinion the values obtained by Caspari and Staudinger may be close to the truth. It is for this reason no molecular weight values are given in this paper. The intrinsic viscosity data will suffice to indicate the molecular weights if the formula $(\eta) = 5 \times 10^{0.5} M$ is employed. This reflects the results obtained by Caspari which the author thinks are probably the most dependable in view of the procedure used in his measurements. Further work must be carried out to determine the true molecular weight of rubber and the most reliable relation between viscosity and molecular weight.

Carter, Scott and Magat[16] from viscosity and osmotic molecular weight measurements on fractions from smoked sheets found the relation $(\eta) = 5.02 \times 10^{-4} M^{0.667}$ and this has been employed by various investigators recently. This relation leads to values more than 10 times higher than Caspari's or

Staudinger's early values, for the molecular weight of sol rubber from crepe or smoked sheets.

SUMMARY

A special procedure of collecting rubber latex directly from the tree by dropping it directly into alcohol to coagulate and preserve it has been described.

The color, hardness, solubility in benzene or chloroform and viscosity of the soluble portion of this alcohol-coagulated rubber has been found to vary widely in the case of rubber from 24 individual trees in a Costa Rica rubber estate.

While it is shown that rubber from individual trees show wide variations, the results from bulked latex and crepe are close to the average results found for the 24 trees.

The results from the present investigation show that rubber direct from the tree contains soluble and insoluble fractions like those found in crepe and smoked sheet. Lower polymers in crepe and smoked sheet are also present in the latex as it emerges from the tree. It was found that some trees yielded a rubber almost completely soluble in benzene or chloroform, while in others, the soluble portion was as low as 61 per cent, with the average being 80 per cent. High viscosity of the sol and insoluble gel both lead to hard tough rubber.

The alcohol coagulums varied widely in color from almost white in the case of some trees to various shades of cream in most of the others. A new and unexpected finding was that four of the 24 trees yielded a distinctly grey mottled coagulum. This grey color apparently comes from the presence of clotted grey lutoids not apparent in the latex itself.

The constitution of sol and gel rubber is discussed and data are presented on the solubility and viscosity of the solutions obtained from the gel fraction. From these data it is concluded that the difficultly soluble gel is a three dimensional network structure with either oxygen or carbon-to-carbon linkages between the polyisoprene chains.

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γ-IRRADIATION OF RUBBER AND STYRENE. GRAFT POLYMER FORMATION *

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In a previous investigation[1], radiation was used to initiate a free radical reaction in a rubber-monomer mixture, the main object being the separation and characterization of the polymeric products. For this, the most suitable monomer was methyl methacrylate. The present investigation extends this work to quantitative aspects of energy absorption, and, for experimental reasons, styrene is a more convenient monomer.

The polymerization of styrene on exposure to high energy radiation has been previously studied[2,3,4]. Styrene has also been polymerized in the presence of polyisoprenes[5], including rubber[6,7], but not by irradiation.

EXPERIMENTAL MATERIALS AND METHODS

An acetone-extracted rubber[1] (0.4% O, 0.3% N, 1.5% extract) had a limiting viscosity number of 386 g^{-1} ml benzene and an osmotic molecular weight, ca. 10^6. A crosslinked rubber was prepared by shearing in 2% dicumyl peroxide ($[\eta]$ of mixture = 248 g^{-1} ml benzene) and heating under pressure for 1 hour at 140° C. Pieces were acetone-extracted in nitrogen for 48 hours and dried in vacuo (0.9% O).

Styrene (Forth Chemicals Ltd.) and methyl methacrylate (Kallodoc of I.C.I. Ltd.) were washed with 10% aqueous sodium hydroxide, with distilled water, and then dried over sodium sulfate.

Solvents were of analytical grade. Samples of *tert*-dodecyl mercaptan and hexachloroethane were purified, respectively, by distillation under reduced pressure and by recrystallization.

PREPARATION OF SAMPLES

Monomer, containing any additive, was run on to degassed rubber in a tube immersed in liquid nitrogen. During degassing in two cycles of pumping, melting, and freezing, the monomer was uniformly imbibed on the rubber surface. Rubber and monomer, separately, were also degassed. All tubes were sealed at ca. 10^{-4} mm Hg pressure. Samples were kept for from one to three days at room temperature plus from 3 to 7 days at −30° before irradiation.

IRRADIATION

The source at Wantage Radiation Laboratory (A.E.R.E.) comprised four similar lines of Co-60 (total ca. 4700 curie) symmetrically spaced around the exposure zone, in which the field intensity ranged from 1.48 to 1.59 (average 1.50) × 10^5 rep/hour [$G(Fe^{+++}) = 15.6$]. Data presented for quantitative

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TABLE I

POLYMERIZATION OF METHYL METHACRYLATE

Dose, rep $\times 10^{-4}$	Field intensity, rep/hr: 6×10^4 Conversion, %	6×10^4 $[\eta]$, g^{-1} 100 ml	4×10^4 Conversion, %	4×10^4 $[\eta]$, g^{-1} 100 ml
0	1.5	—	1.3	—
1.0	6.1	12.4	0.9	—
2.0	8.0	10.1	1.7	—
3.0	11.0	6.83	—	—
4.0	13.2	7.72	3.2	10.0
6.0	23.3	6.19	5.4	9.3
8.0	—	—	5.0	6.04
10.0	95.2	5.19	5.4	6.15
20.0	—	—	9.5	3.2

comparison were obtained by simultaneous exposure. Exposures of greater than 5 hours were from time to time interrupted for about 3 minutes in order to remove samples from the source, a time correction being made. The ambient temperature in the exposure zone was about 34° C.

POLYMERIZATION OF MONOMER

The ampoules were opened from one to four days after irradiation. Unreacted monomer was stripped from irradiated samples *in vacuo*, first at room temperature and then at 70° C. The gravimetrically determined extent of polymerization was corrected for residual styrene, in the presence of soluble polymer, by ultraviolet spectroscopy[8].

INSOLUBLE FRACTION

The insoluble factions of the gross polymer after 5 days at 25° C in chloroform was estimated by gravimetric analysis of the sol passing through lens tissue paper.

Swelling index.—When the insoluble fraction was a well defined gel, a swelling index, the number of milliliters of solvent imbibed per gram of gel, was determined gravimetrically.

TABLE II

POLYMERIZATION OF STYRENE

System	Dose, rep $\times 10^{-4}$	Conversion, %	$[\eta]$, g^{-1} 100 ml	$G(p, s)$ values
Styrene	2.29	8.0	0.376	0.77
	2.70	9.0	0.361	0.77
	3.08	10.0	0.389	0.68
	5.81[a]	—	0.373	
	5.81[b]	—	0.337	
Styrene with 2% hexachloroethane	2.29	14.8	—	
	2.70	16.7	0.235	
	3.08	20.0	0.285	
	5.81	—	0.361, 0.410	
	5.81[b]	—	0.303	

[a] Osmotic molecular weight = 43,000, $[\eta]$ calculated molecular weight = 46,000.
[b] Air was admitted to contents of tube immediately after irradiation.

Ozonolysis[9,1].—The polystyrene in the gross, styrene-free product was separated by ozonolytic destruction of the rubber. Owing to the presence of an insoluble fraction, small pieces of polymer survived this treatment. When the ozonized solution was stirred into methanol, these pieces formed into a lump which was easily removed. The remaining precipitate constituted not less than 90% of the polystyrene initially present. Redissolution of this and further ozonolysis gave a recovery > 98%.

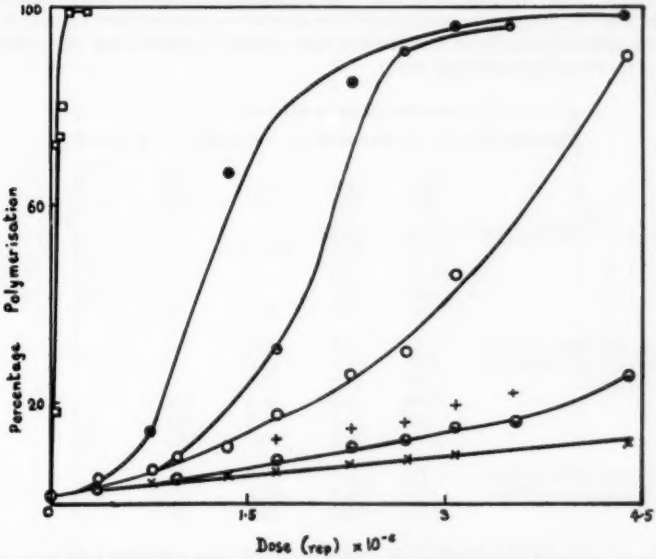

FIG. 1.—Rate of styrene polymerization. Dose rate: 1.5 × 10⁶ rep/hr.: (○) extracted rubber-50% styrene; (◒) the same with 0.5% dodecyl mercaptan on monomer; (◓) the same with 2% C_7Cl_8 on monomer; (●) extracted rubber-22% styrene; (×) styrene; (+) styrene with 2% C_7Cl_8; (□) extracted rubber-50% methyl methacrylate.

SEPARATION OF FREE PLASTOMER FROM NETWORK

About 0.5 g polymer (in pieces of ca. 0.07 g) was kept in 50 ml benzene for 7 days at 25° C. By this time, the sol fraction had attained an almost constant concentration of polymer, from which could be calculated the percentage of plastomer which is free, i.e., not combined with the crosslinked rubber. A correction was made for soluble rubber.

Limiting viscosity number and osmotic molecular weight.—These measurements were made as previously described[1].

Equilibrium swelling of rubber. Samples were immersed in *n*-decane for 72 hours at 25° C. The volume fraction of rubber in the swollen polymer, V_r, was determined gravimetrically.

EXPERIMENTAL RESULTS

Rate of polymerization and viscosity data for methyl methacrylate and styrene are given in Tables I and II, respectively. From the initially linear plot in Figure 1 the rate of polymerization of styrene was calculated to be 0.94

$\times 10^{-5}$ m/l/sec. The same figure also shows how the rate of polymerization of styrene is increased by hexachloroethane and by the two concentrations of rubber. The much more rapid polymerization of methyl methacrylate in rubber is included for comparison. The rate of polymerization of styrene in the presence of rubber is increased by hexachloroethane and retarded by *tert*-dodecyl mercaptan. Data on the polystyrene formed in the presence of rubber and separated by ozonolysis are given in Table III, together with data on gel formation. The swelling indexes of the insoluble fractions from the original rubber and the polymeric products of the shorter exposures were usually erratic and irreproducible. With a sufficient dose a clearly defined gel was produced with a reproducible swelling index.

TABLE III

POLYMERIZATION OF STYRENE IN PRESENCE OF RUBBER

System	Dose, rep $\times 10^{-6}$	Conversion, %	Gel, %	Gel swelling index	Polystyrene, $[\eta]\ g^{-1}$ 100 ml	$G(p, m)$ values
Rubber plus 50% styrene	1.73	17.5		—	0.72	0.45
	2.29	25.4	25–30	—	0.70	0.55
	2.70	30.4		—	0.78	0.45
	3.08	44.8		—	1.04	0.37
	4.38	86.5	46.1	56.1		
Rubber plus 50% styrene with 0.5% *tert*-dodecyl mercaptan	1.73	9.4	6.8	—		
	2.29	11.8	12.0	—		
	2.70	13.0	13.2	—		
	3.08	15.3	15.5	222		
	3.52	16.5	19.5	174		
	4.38	19.5	20.7	159	0.27	
Rubber plus 50% styrene 2.0% hexachloroethane	1.73	31.4	28.4	116		
	2.70	91.0	52.2	36.3	0.89	
	3.52	96.0	66.1	23.2		

The G value is the number of chemical events, specified in brackets, which occur per 100 e.v. of absorbed energy. The energy deposition in 1 g water produced by a field intensity of 1 rep is taken as 6.08×10^{13} e.v. Corresponding to the number of electrons per gram relative to water, depositions have been calculated for styrene and rubber of 5.9 and 6.1×10^{13} e.v./g/rep, respectively.

$G(p, s)$ values (i.e., polystyrene in styrene) were calculated from the number of polystyrene molecules formed per gram of monomer in the bulk polymerization. The relationship[10] $\log M = (\log [\eta] + 3.832)/0.73$ was confirmed experimentally by osmotic molecular weight determination and used to estimate the number-average molecular weight, M. $G(p, m)$ values (i.e., polystyrene in the mixture) were similarly calculated after removal of rubber. In this case, both the energy absorption and the number of molecules is referred to 1 gram of mixture (see Tables II and III).

CROSSLINKING OF RUBBER

Mullins[11] has empirically related V_r with the network constant C_1. Provided a correction is made for the finite initial molecular weight of the rubber $C_1 = (\frac{1}{2})\ \rho\ RTM_c^{-1}$. For the present C_1 values this correction would involve an increase of only from about 3 to 6% and was not applied. The number of crosslinks per gram of gel is given by $\frac{1}{2}M_c^{-1}N$, where N is the Avogadro num-

ber[12]. Calculations were made as though the rubber comprised entirely gel when the amount involved was not less than 95%. This overestimates the actual crosslinking density and qualitatively compensates for not applying the initial molecular weight correction.

The $G(X)$ value was calculated as

$$\frac{\text{number of crosslinks per gram}}{\text{energy absorbed (in e.v.) per gram}} \times 100 = \left(\frac{NC_1}{\rho RT}\right)\left(\frac{100}{6.1 \times 10^{13} D}\right)$$

where D is the dose in rep, and a mean value of 0.92 was taken for the density of the rubber, ρ.

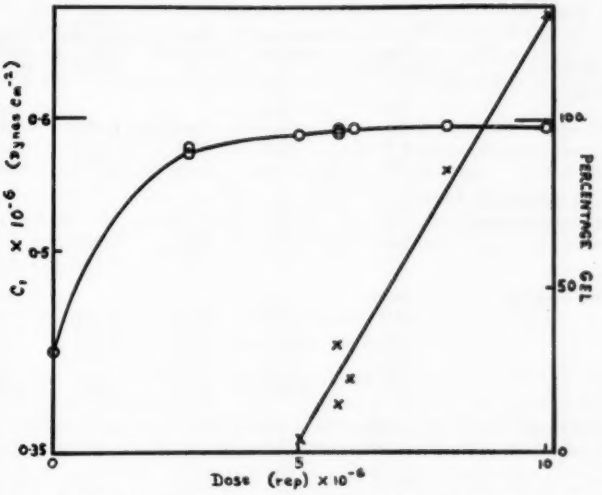

FIG. 2.—Swelling of irradiated rubber in *n*-decane: (×) values of network constant, C_1; (○) percentage gel.

$G(X)$ up to 6 M rep was calculated as 3.04. This includes the relatively few crosslinks formed by acetone extracting rubber and drying *in vacuo*.[13] $G(X)$ in the range of from 6 to 10 M rep was calculated from Figure 2 as 2.97.

FREE POLYSTYRENE

The amount of free polystyrene formed by polymerization in the presence of crosslinked rubber, and, in some cases, viscosity data, is shown in Table IV. Incidentally, the table includes swelling data for the interpolymer networks.

DISCUSSION

The polymethyl methacrylate formed after a few per cent conversion of monomer has a very high limiting viscosity number (Table I). With longer exposures, the viscosity is markedly decreased, probably because of radiation-induced degradation[14]. Apparently, the long period which elapses between the preparation and testing of samples introduces factors which completely

obscure the simple dependence of molecular weight on field intensity which has been previously reported[3,15,16].

Styrene proved to be a more satisfactory monomer for the present investigation. A rate of polymerization of 1.06×10^{-5} m/l/sec calculated for a field intensity of 1.9×10^5 rep/hr, from the data in Figure 1 is in good agreement with the previously reported experimental value of 1.01×10^{-5} m/l/sec[3,17]. There is also reasonable agreement with previously reported viscosity data. It has not been established whether this slightly increased rate of polymerization

TABLE IV

POLYMERIZATION OF MONOMER IN CROSSLINKED RUBBER

System	Dose, rep $\times 10^{-6}$	Polymerization %	Free plastomer, %	$[\eta]$ Soluble plastomer, g^{-1} 100 ml	Swelling index of network
50% styrene	0	0.5			
	1.7	9.4			5.02
	4.9	54.0	15.5	0.587	5.08
	7.7	78.5	13.7	—	4.90
	9.0	97.5	14.8	0.477	4.80
50% styrene with 0.5% *tert*-dodecyl mercaptan	3.2	14.3	78.5		5.11
	4.8	18.1	82.2		4.88
	7.6	30.0	83.9	0.165	5.13
	9.0	43.0	74.3	0.181	5.01
50% styrne with 2% C_2Cl_6	0.85	5.4			5.01
	3.8	88.5	23.2	0.521	4.83
	4.4	94.3	21.8	0.462	4.95
	4.9	93.4	21.4	0.395	4.95
	7.6	98.8	23.5	—	4.64
	9.0	100.5	26.4	0.381	4.66
50% methyl methacrylate	0.033	1.5	—		5.07
	0.067	29.5	2		4.64
	0.10	42	2		4.80
	0.12	70	2		4.70
	0.20	80	2.3		4.69
	0.47	100	4.6		4.65

is due to some post-irradiation polymerization occurring when the mixtures are kept for several days *in vacuo*. A possibly related effect is the indication that lower molecular weight polystyrene is formed when air is introduced into the reaction mixture immediately after irradiation (Table II).

ENERGY DEPOSITION FROM γ-RADIATION IN MIXTURES

Co-60 photons interact with electrons, in atoms of low atomic number, by Compton scattering. The dose depends on the number of recoil electrons and is thus determined by the intensity of the radiation and the number of electrons in the sample. As is well known, the dose in a mixture comprising weight fractions w_1 and w_2 of hydrocarbons 1 and 2, respectively, would be given by the expression:

$$\left[\frac{w_1 n_1}{M_1} + \frac{w_2 n_2}{M_2}\right] \frac{M_0}{n_0} CD \text{ e.v./g} \qquad (1)$$

n_0, n_1, and n_2, being the number of electrons per molecule of water and the two components, respectively. The M terms are the corresponding molecular weights and D is the field intensity in rep, 1 rep being taken to produce an energy deposition of C e.v./g in water.

The sharing of this dose between the components may be calculated by application of the assumption of Burton et al.[18], for which experimental justification was subsequently provided[19], that each hydrocarbon component absorbs energy from an electron beam in proportion to its electron fraction. The electron fraction of component 1 is given by

$$w_1 n_1 M_1^{-1} (w_1 n_1/M_1 + w_2 n_2/M_2)^{-1} \quad (2)$$

Therefore, the energy absorbed by this component for a dose of D rep is given by the product of Equation (1) and (2), $w_1 n_1/M_1(M_0/n_0)(CD$ e.v./g). Comparison with expression (1) shows that a component of a mixture absorbs energy at the same rate from the recoil electrons as it would do alone in the same γ-field.

Condensed phase reactions, including polymerizations, have been analyzed quantitatively in terms of the free radicals which may arise from the ions and excited molecules formed in the track of the recoil electrons. If the radiolysis of each component of the mixture proceeded independently, then an energy deposition of 100 e.v. would yield $(\theta_1 G(r_1) + \theta_2 G(r_2))$ radicals, where the θ and $G(r)$ terms refer to the electron fractions and G(radical) values of the components, respectively.

YIELD OF RADICALS FROM RUBBER ON γ-IRRADIATION IN THE PRESENCE OF STYRENE

It has been proved that the radiation-induced polymerization of styrene is propagated by a monoradical[4]. Neglecting any transfer reactions and accepting that termination of polymerization occurs by combination of polymeric radicals, then there would be two polymerization-initiating radicals for each molecule of polystyrene. The number of polystyrene molecules has been calculated from a limiting viscosity number-osmotic molecular weight relationship, which has been verified experimentally (cf. Table II). It is also assumed to apply for polymer formed in the presence of rubber at the lowest conversion (17.5%) at which sufficient polystyrene could conveniently be separated. From this value $G(p, m)$ is calculated as 0.45 (Table III).

The $G(p, s)$ value, from Table II, is 0.77 at the lowest conversion of 8.0%. The derived value for polymerization-initiating radicals of $2G(p, s) = 1.54$ may be compared with the value of 0.49 as calculated from the rate of initiation of polymerization of 1.83×10^{-8} m/l/sec[17]. Corresponding values calculated from the previously reported similar data[3] are $2G(p, s)$ at 12.6% conversion = 0.98 and, from the rate of initiation, 0.46. Other values of 0.22 and 1.6 have been reported[4,20], but for very different experimental conditions. The value calculated from the yield of polystyrene is preferred here beacuse it can be derived for the mixture.

The G value for formation of polymerization-initiating radicals from the rubber in the mixture, $G(i.r.)$, may be calculated from the above values, provided the distribution of absorbed energy between rubber and styrene is known. For simplicity, the approximation will be made that the rubber and styrene absorb equal amounts of energy. Then, for a deposition of 200 e.v. in the

mixture $4G(p, m)$ initiating radicals are formed of which $2G(p, s)$ come from styrene and $G(i.r.)$ from rubber, i.e., $4G(p, m) = 2G(p, s) + G(i.r.)$. This equation is used for data obtained at 17.5% conversion in the mixture on the view that replacement of this amount of styrene by polystyrene should not seriously affect the rates of radical formation and polymerization.

The yield of initiating radicals from rubber is, thus, $G(i.r.) = 0.26$. This is much too low by comparison with that from styrene, $2G(p, s) = 1.54$, in view of the general rule that olefins give a much higher yield of radicals on radiolysis than do aromatic compounds[21]. Even then, the value may be an overestimate, as it would include any additional polystyrene molecules formed by transfer with the rubber, i.e., $G(p, m)$ overestimated.

An assessment of the G (radical) value for rubber, when irradiated alone, may be made from its $G(X)$ value. In general, $G(x)$ values are largely independent of the intensity or even the nature of the radiation. However, a previous value of 2.3 reported for pile radiation[22] was obtained under such different circumstances that it is not properly comparable. The present value of 3.0 has been established only for the relatively limited dose range of interest in the study of polymerization. Radiation crosslinking of rubber is predominantly, at least, a free radical reaction[23]. Therefore, assuming that, as in thermal crosslinking with peroxides[12], two radicals combine to form one crosslink, then $G(\text{radical}) \sim 6$.

There are two factors which might contribute toward the discrepancy between the yield of radicals from rubber when irradiated alone and the number which initiate polymerization in the mixture. Firstly, the radicals are formed in small but dense clusters, so that even a large concentration of radical acceptor may not completely prevent their combination. Secondly, the radicals may be so unreactive that even some of those which escape from the clusters may survive without reaction with the styrene to eventually combine. In fact, it would be expected that, even together, these factors would not be sufficiently important to account for a discrepancy of this magnitude. Concerning the first point, it would seem that at least two-thirds of the radicals formed by radiolysis of rubber are available to a radical acceptor[23]. Concerning the other, it is known that even the least reactive radicals (allylic) derived from polyisoprenes can initiate the polymerization of both styrene[6,7] and of the less reactive monomer, methyl methacrylate[24].

From these considerations its seems likely that the G (radical) value itself is lower for rubber in the mixture. Further evidence is provided by a comparison of gel formation in rubber alone and in the mixture.

As rubber absorbs energy at the same rate in the mixture as on its own, then, if it had the same G (radical) value, gel formation should be comparable. Yet while in the absence of styrene the initial gel fraction of about 30% increases rapidly on exposure (Figure 2), a similar trend is apparent, in its presence, only after an exposure of 20 hours (Table III).

PROTECTION OF RUBBER BY ENERGY TRANSFER TO STYRENE

The decreased number of radicals formed from rubber in the presence of styrene, on γ-irradiation, parallels the decreased yield of hydrogen from cyclohexene in the presence of benzene, on irradiation with a beam of electrons. Manion and Burton[18] concluded that their results for the latter system were consistent with a mechanism whereby excited molecules of cyclohexene, which otherwise could lead to hydrogen formation, transfer excitation energy to

benzene where it could be dissipated without chemical consequences. However, they did not exclude the possibility of an alternative radical mechanism of protection. In fact, although many examples of protection by intermolecular energy transfer have been proposed, experimental evidence has been provided to demonstrate the inadqeuacy of an alternative radical mechanism only for the protection of cyclohexene by deuterobenzene[19].

The present example is important because a free radical mechanism of protection is untenable. It provides a verification of the importance of energy transfer in radiation chemistry under very different experimental conditions from those pursued by Burton et al. (see ref. 21).

THE POLYMERIC PRODUCTS

On account of the similar solubility of rubber and polystyrene, extraction and precipitation techniques for separating polystyrene from the gross polymer are not entirely satisfactory[6]. Neither is selective crosslinking of rubber by heating with a peroxide[7]. Therefore, it was preferred to irradiate styrene imbibed by an already crosslinked rubber so that the free plastomer could be determined simply by partition of sol in benzene. The amount of the plastomer which is free, i.e., uncombined with the rubber, was about 15% as compared with only a few per cent in the case of polymethyl methacrylate (Table IV). This separation technique is, in principle, not entirely suitable for polymethyl methacrylate because enormously large molecules are formed which might not diffuse satisfactorily from the network. However, it has been previously established, checking by the precipitation technique, that the yield of free polymethyl methacrylate is, indeed, quite small[1]. The free plastomer content might account for the difference in appearance of the products. Those from methyl methacrylate are almost as clear as the initial transparent crosslinked rubber but those from styrene are quite opaque. Opacity is probably due to microphase separation which can occur when the plastomer is free to diffuse. A related phenomenon is that rubber/polymethyl methacrylate products become more opaque on immersion in acetone, presumably on account of the increased mobility of the plastomer in the swollen polymer. This effect is even more marked with the present products because they are initially transparent. They regain their transparency on removal of acetone.

It has been suggested that graft polymer should be formed on irradiation of a mixture of polymerthyl methacrylate and styrene because the polymer has a much higher G (radical) value[17]. This can be generalized as a useful criterion for obtaining a high yield of interpolymer but, in view of the demonstrated protection of rubber by styrene, needs to be qualified as *applying in the mixture*. Without this qualification it would be wrongly predicted that, as the G (radical) value of methyl methacrylate is some tenfold that of styrene, it should yield more free plastomer than styrene. This prediction would be further strengthened by secondary considerations. Firstly, polymethyl methacrylate radicals partially disproportionate, so that, if only one of the pair is already combined with rubber, free plastomer may result. Secondly, free polymethyl methacrylate may be formed through its radiation-induced fracture from the interpolymer, while, by contrast, free polystyrene may be subsequently combined, although to a small extent, by radiation crosslinking (cf. $G(X)$ of the order 0.02)[25].

Consideration of the fairly high ratio of initially nonpolymeric to polymeric radicals (i.e., $(0.5G(i.r.) + 2G(p, s))/0.5G(i.r.) \sim 13$, assuming half the radicals

from rubber to be nonpolymeric) helps to account for the greater amount of free plastomer from styrene. However, as only some 15% of the plastomer is free, it is supposed, as previously, that reaction of initially nonpolymeric radicals with the rubber to form further grafting sites is important. Advantage has been taken of this reaction to increase the rate of polymerization without proportionately increasing the amount of free polystyrene. For this purpose, hexachloroethane was included in the mixture as an example of an additive with a very high G (radical) value. As would be expected, it leads to an increased rate of polymerization, both in the absence and presence of rubber (Figure 1). However, Table IV shows that the amount of free polystyrene is increased only to some 23%. With the efficient transfer agent, *tert*-dodecyl mercaptan, about 80% of the polystyrene was free.

The increasing viscosity of polystyrene formed in the presence of rubber, even in the early stages of conversion, together wiht the increasing rate of polymerization under conditions where rise of temperature would be small[3] is probably due to a Trommsdorf gel effect. Similar, but much more marked, observations with methyl methacrylate and, in particular, the enormous molecules formed, may involve further factors as indicated by the results of Table I.

SYNOPSIS

Styrene, styrene mixed with rubber, and rubber alone have been exposed to γ-radiation from Co-60. The G value for polymerization-initiating radicals formed from rubber in the mixture, $G(i.r.) = 0.26$, has been calculated from corresponding values obtained by estimation of the number of polystyrene molecules formed in styrene and in the mixture. A G (radical) value for rubber when irradiated alone, $G(r)$, has been assessed from a G (crosslinking) value, $G(X)$, which was determined under closely similar experimental conditions, as $G(r) = 2G(X) \sim 6$. The large discrepancy between $G(r)$ and $G(i.r.)$ cannot be explained satisfactorily on the supposition that radicals formed from rubber have a low efficiency in initiating the polymerization of styrene. Therefore, it is argued that the $G(r)$ value itself is lower in the mixture. Evidence for this argument is provided by the lower rate of gelling in the mixture. This protection of rubber by energy transfer to styrene is an important example since in only one previous case has experimental evidence been provided to exclude an alternative radical mechanism. By polymerization in the presence of crosslinked rubber, uncombined polystyrene could be readily partitioned into the sol fraction by equilibriation of the gross polymer in benzene. About 15% of the polystyrene was free. Hexachloroethane was chosen as an example of an additive with a high G (radical) value. Ax would be expected, it increases the rate of polymerization but does not lead to a correspondingly large amount of free polystyrene (about 23%). Graft polymer formation from styrene and methyl methacrylate is compared and attention is drawn to the importance of the formation and subsequent reactions of initially nonpolymeric radicals in determining the proportion of free plastomer.

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POLAROGRAPHIC DETERMINATION OF ACCELERATORS, ANTIOXIDANTS, AND OTHER RUBBER CHEMICALS. I.*

F. MOCKER

VEITH-GUMMIWERKE A.-G., HÖCHST, ODENWALD

Polarography appears to be little known when compared with the many rapid analytical procedures such as potentiometry, fluorescence analysis, colorimetry, or paper chromatography which find wide use in the rubber laboratory. However, polarography as developed by Heyrovský[1] is particularly suited to a long series of daily routine analyses because this method permits the examination of both organic and inorganic substances in the least time and with the greatest accuracy. Proske's[2] work initially showed how versatile in the rubber laboratory was this elegant, accurate, and rapid method. The scope of some preliminary experiments convinced the writer that polarography, as an analytical tool, would make possible the detection of a large number of accelerators, antioxidants, retarders, etc., both qualitatively and quantitatively.

PRINCIPLE OF THE METHOD

During the electrolysis of a solution between two mercury electrodes with increasing potential the presence of various substances cause a sudden increase in the current at certain potentials. While this decomposition or depolarization potential is qualitatively characteristic for a substance, the magnitude of the current serves as a quantitative test. Every change in concentration during the electrolysis will naturally introduce errors. Therefore, the current voltage curves (c. v. curves) must be taken under conditions of a minimum current that will satisfy the analytical requirements yet will not cause changes in concentration. Moreover, the dropping mercury electrode is used in order to assure an electrode of uniform quality. Through the constant renewal of its smooth surface the dropping mercury electrode offers the possibility of measuring c. v. curves reproducibly. The relatively large surface of the pool of mercury on the bottom of the electrolytic cell serves as the opposite electrode. Figure 1 shows such an arrangement by which it is possible to perform analyses with a limit of error of $\pm 1\%$ on a few milliliters of dilute solutions with concentrations of 10^{-4} mole/l when noninterfering conducting salts are added to the solution to reduce the internal resistance.

Such a sensitive analytical method naturally requires a correspondingly sensitive measuring arrangement. Figure 2 shows the principle of measurement and illustrates the Poggendorf compensating circuit. In this case, both increasing current and rising potential are measured simultaneously.

Polarographs of substantially automatic design are available to the practicing chemist. These instruments make it possible to record polarograms photographically as shown in the schematic diagram of Figure 3. Recently polaro-

* Translated by Henry J. Kehe from *Kautschuk und Gummi* 11, WT281-292 (1958).

graphs have been developed which trace the curve on a recorder chart. This design reduces the time-consuming development of the polarogram that causes a great loss of time in relation to that required for doing the analyses and plotting the curves.

A polarogram will now be schematically prepared and briefly described (Figure 4). In this figure, the potential is plotted on the abscissa against the current on the ordinate. Upon reaching the depolarization potential, the cur-

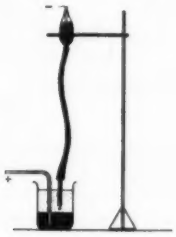


FIG. 1.—Arrangement of electrolytic apparatus.

rent increases rapidly in the form of a step or wave and persists at this limiting value (limiting current, diffusion current) which is directly porportional to the concentration of a substance with a specified drop time of the electrode.

While the reduction of metal ions at the cathode is primarily decisive for the polarogram with inorganic substances, for organic materials there begins a cathodic reduction which in a similar manner, is characteristic for that material.

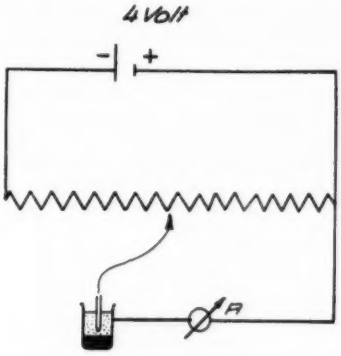


FIG. 2.—Principle of measurement.

For the qualitative interpretation of the polarogram it is necessary to consider as depolarization-potential, that potential at which the step exhibits its midpoint (halfwave potential), while for the quantitative analysis only the wave height needs to be measured with regard to the sensitivity of the galvanometer and compared with a calibration curve taken from many solutions under precisely the same conditions.

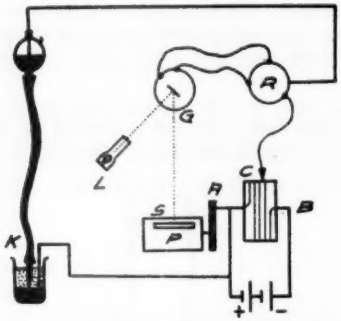


FIG. 3.—Schematic diagram of a polarograph with photographic recorder. A—B Resistance wire on a drum (Kohlrausch-Trommel). C—Slide contact. G—Reflecting galvanometer. K—Electrolytic cell. L—Galvanometer lamp. P—Photographic drum. R—Sensitivity switch. S—Slit in photographic drum.

DETERMINATION OF 2-MERCAPTOBENZOTHIAZOLE (MBT)

Proske[3], Sartori and Liberti[4] as well as Fedoronko and Zumann[5] have studied the polarography of MBT. In the polarogram, definite steps appear for it. Their positions depend on the composition and pH of the supporting electrolyte as well as on the concentration of the MBT.

The use of solutions containing various amounts of gelatine revealed that the quantitative determination of MBT in pure solutions is feasible without difficulty with an accuracy of $\pm 1\%$. The solutions must have the pH maintained at 7.8, and concentrations held within narrow limits.

Experimental details.—The galvanometer used to plot the c. v. curves has a sensitivity (E) of $1.85 \cdot 10^{-6}$ amp/mm at a distance of 65 cm exposed to the atmosphere. The reduction potentials were measured against a 1 N calomel electrode.

Current supply	4 V storage battery
Drop time	1.7 seconds
Temperature	20° C
Initial potential for all c. v. curves	0 V

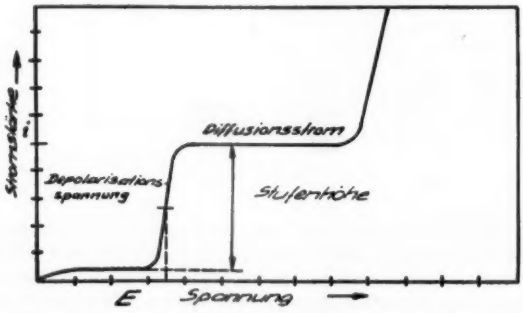


FIG. 4.—Schematic description of a polarogram. Abscissa: voltage; ordinate: current. The first plateau is denoted depolarization potential and the second diffusion current. The arrow signifies wave height.

The MBT was dissolved in purest methanol and added to the supporting electrolyte. The following solutions served as supporting electrolytes

1.	HCl 2*N*	100 ml
	KCl 2*N*	100 ml
	NH_4Cl 4*N*	500 ml
	Gelatine solution 0.91%	220 ml
	Methanol	880 ml
2.	KCl 2*N*	100 ml
	NH_4Cl 4*N*	500 ml
	Gelatine solution 0.63%	320 ml
	Methanol	880 ml
3.	NaOH 2*N*	100 ml
	NH_4Cl 4*N*	500 ml
	Gelatine solution 0.63%	320 ml
	Methanol	880 ml
4.	NaOH 2*N*	200 ml
	NH_4Cl 4*N*	500 ml
	Gelatine solution 0.91%	220 ml
	Methanol	880 ml

The methanolic MBT solution (20 ml) was added to 50 ml of each of the above supporting electrolytes. *In all polarograms reproduced here the potential gradient (abscissa) is 0.2 volt per division.*

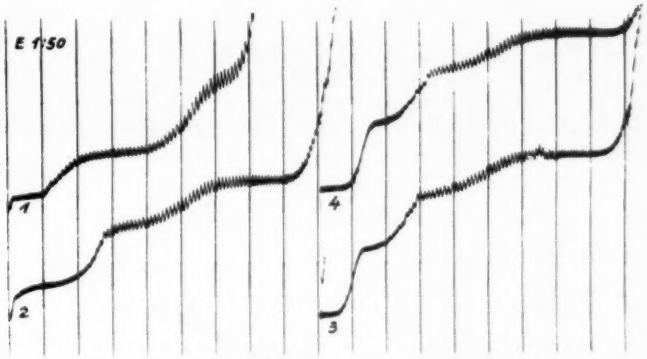


FIG. 5.—Polarograms of MBT in supporting electrolytes 1—4 (see Table I).

TABLE I (for Figure 5)

Curve	MBT, mole/l	Supporting electrolyte	pH	Sensitivity	Reduction potential
1	$1 \cdot 10^{-2}$	1	1.6	1:50	−0.232
2	$1 \cdot 10^{-2}$	2	5.4	1:50	−0.334
3	$1 \cdot 10^{-2}$	3	7.8	1:50	−0.167
4	$1 \cdot 10^{-2}$	4	8.1	1:50	−0.197

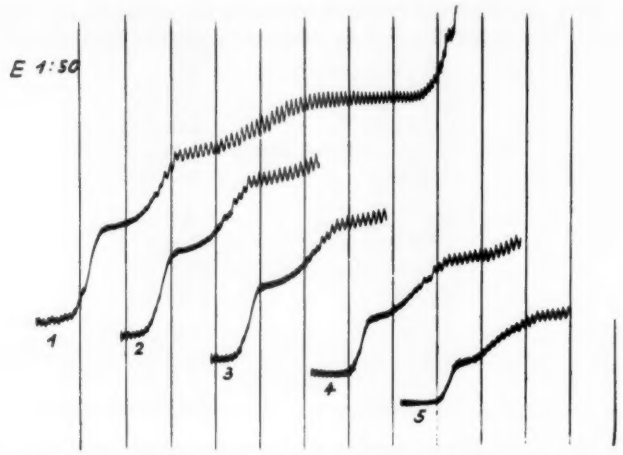


FIG. 6.—Polarograms of MBT in supporting electrolyte No. 3. Concentrations from Table II.

TABLE II (for Figure 6)

Curve	MBT, mg/ml	Sensitivity
1	1.874	1:50
2	1.669	1:50
3	1.429	1:50
4	1.154	1:50
5	0.834	1:50

For MBT the polarograms in Figure 5 show the c. v. curves from the data recorded in Table I. This table also tabulates the reduction potentials of MBT observed at the various pH values of the solution. The curves also reveal that the wave height of the MBT solution with a pH 7.8 is satisfactory for quantitative evaluation.

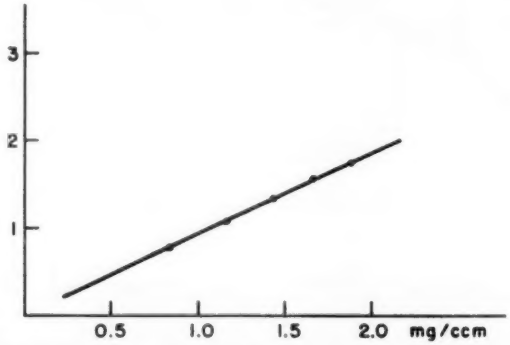


FIG. 7.—Calibration curve for determination of MBT. Abscissa: concentration in mg per ml; ordinate: wave height in cm at E 1:50.

The polarograms in Figure 6 show the previously mentioned but weak dependence of the reduction potential on the concentration of MBT. Yet in a determination of the concentration of MBT the phenomenon is without effect. In order to stay within the customary tolerance of $\pm 1\%$ required in polarographic studies the concentration range must be kept small.

Plotting the heights of the reduction waves from Figure 6 against the indicated concentrations in Table II gives the calibration curve (Figure 7) for MBT at a galvanometer sensitivity of 1:50. The calibration curve is a straight line. As long as drop time, galvanometer sensitivity and temperature remain constant, this calibration is valid and reproduible for a given capillary.

TABLE III

DETERMINATION OF THE LIMIT OF ERROR ACCORDING TO THE CALIBRATION CURVE IN FIGURE 7

Concentration of MBT, mg/ml		Error, %
Theoretical	Observed	
0.850	0.848	−0.2
0.100	0.100	0.0
1.250	1.261	+0.9
1.400	1.398	−0.1
1.600	1.597	−0.2
1.700	1.704	+0.2
2.000	2.002	+0.01

The determination of the limits of error in the anlysis of pure MBT solutions by means of the calibration curve under the specified experimental conditions gave the results shown in Table III.

If determination of other ratios of concentration are under consideration, then—as additional experiments revealed—only a change in galvanometer sensitivity is needed as the wave height is proportional to the change in sensitivity at constant concentration.

Determination of MBT in masterbatches.—Masterbatches with compositions shown in Table IV were sheeted out very thin and extracted for 16 hours with

TABLE IV

COMPOSITION OF THE MASTERBATCHES

	1	2	3	4
Crepe rubber	100	100	100	79.90
MBT	5	10	25	20.00
Identifying dye	—	—	—	0.08

pure methanol in a Soxhlet. The extract was concentrated to 100 ml; and 20 ml of the extract was diluted with supporting electrolyte 3 (50 ml). A portion (10 ml) was examined polarographically. The slight turbidity caused by mixing the extract with the supporting electrolyte did not interfere with the quantitative determinations. Figure 8 reproduces the observed *c. v. curves.* The results of these experiments lead to the conclusion that the polarographic determination of MBT in masterbatches is a thoroughly satisfactory analytical method (see Table V).

Determination of the zinc salt of MBT.—The lack of a suitable solvent pre-

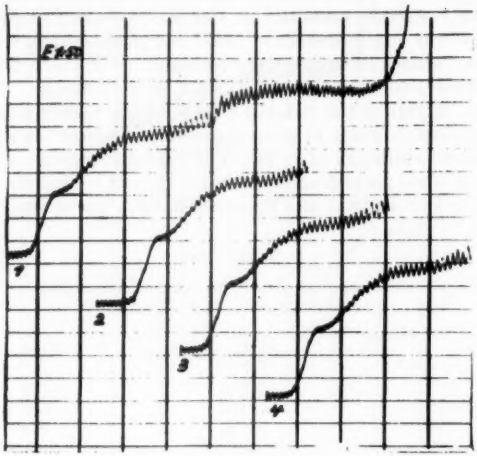
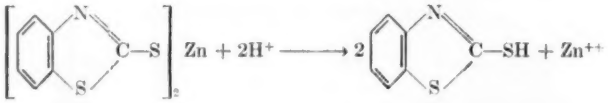


FIG. 8.—Polarograms of MBT. Determination in methanol extracts of masterbatches (see Table V).

TABLE V (for Figure 8)

		2-Mercaptobenzothiazole (MBT)				
				Observed amounts		
Curve	Weight (g) of sample, masterbatch	Amount (mg) in sample	Amt., mg/ml in test solution	in test solution mg/ml	in sample mg	Error, %
1	10.0086	476.6	1.361	1.37	479.5	+0.6
2	5.5056	500.5	1.430	1.42	497.0	−0.7
3	2.5038	500.7	1.430	1.425	498.7	−0.4
4	2.5024	500.5	1.430	1.44	504.0	+0.7

vents the direct polarographic determination of the zinc salt of MBT. However, boiling the zinc salt with acetic acid quickly liberates[6] free MBT.



After precipitating the zinc with hydrogen sulfide, filtering off the zinc sulfide, extracting the filtrate with ether, concentrating the extract, and then diluting it with methanol, the MBT may be determined in the methanol solution. Thereafter it is only necessary to recalculate the observed amount of MBT as the zinc salt. Even in this case the limit of error is below ±1%.

DETERMINATION OF 2-MERCAPTOBENZIMIDAZOLE

Fedoronko and Zumann[5] also studied the polarographic determination of 2-mercaptobenzimidazole. They found in their polarograms well defined

waves that were suitable for analytical purposes. Under the same experimental conditions used for MBT, an analytical method was developed which will be described in the following.

Experimental details.—The c. v. curves were plotted with a galvanometer having a sensitivity (E) of $1.85 \cdot 10^{-6}$ amp/mm at a distance of 65 cm exposed to the air. The reduction potentials were measured against a 1 N calomel electrode. The 2-mercaptobenzimidazole was dissolved in pure methanol and added to the supporting electrolyte. Those used with MBT were employed here. Twenty ml of the methanol solution of 2-mercaptobenzimidazole were added to 50 ml of the individual supporting electrolytes.

The c. v. curves of 2-mercaptobenzimidazole are shown graphically in Figure 9 for the experimental conditions tabulated in Table VI. Table VI also records the observed reduction potentials of 2-mercaptobenzimidazole in solutions at various pH values. Here also at a pH of 7.8 the steps show themselves as satisfactory for quantitative determinations.

The polarograms presented in Figure 10 again show the dependence of the wave heights of the c. v. curves on the concentration of 2-mercaptobenzimidazole in supporting electrolyte 3. The concentrations ranged from 1.031 to 2.222 mg/ml (see Table VII).

In the calibration curve (Figure 11) the wave heights are plotted against the concentration. The limitations given for the calibration curve of MBT (Figure 7) apply here also. The limits of error (see Table VIII) were obtained under these specified experimental conditions. The limit of error in determining 2-mercaptobenzimidazole likewise falls within the $\pm 1\%$ limit.

Determination of 2-mercaptobenzimidazole in masterbatches.—The determination was performed in a manner analogous to that used for MBT master-

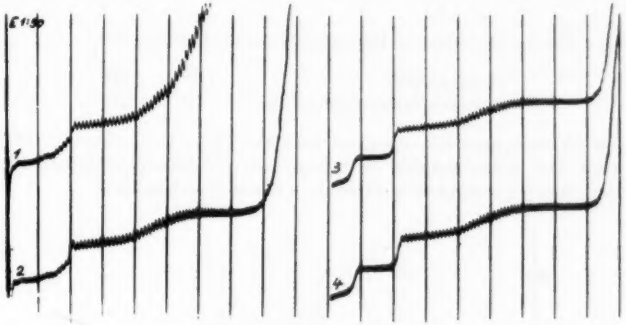


FIG. 9.—Polarograms of 2-mercaptobenzimidazole in supporting electrolytes 1—4 (see Table VI).

TABLE VI (for Figure 9)

Curve	Concentration of 2-mercapto-benzimidazole mole/l	Supporting electrolyte	pH of solution	Sensitivity	Reduction potential
1	$1 \cdot 10^{-3}$	1	1.6	1:50	−0.036
2	$1 \cdot 10^{-3}$	2	5.4	1:50	−0.036
3	$1 \cdot 10^{-3}$	3	7.8	1:50	−0.118
4	$1 \cdot 10^{-3}$	4	8.1	1:50	−0.128

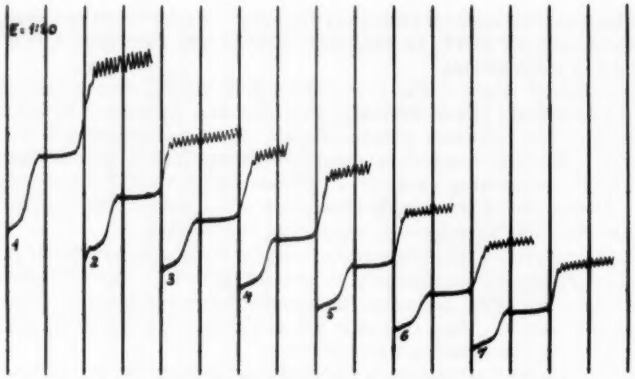


FIG. 10.—Polarograms of 2-mercaptobenzimidazole in supporting electrolyte No. 3 concentrations from Table VII.

TABLE VII (for Figure 10)

Curve	2-Mercaptobenzimidazole, mg/ml	Sensitivity
1	2.222	1:30
2	1.666	1:30
3	1.575	1:30
4	1.478	1:30
5	1.328	1:30
6	1.154	1:30
7	1.031	1:30

batches. The composition of the present masterbatches was:

crepe rubber	100	100
2-mercaptobenzimidazole	10	20

Table IX compares the observed with the theoretical values. The results show that the polarographic determination of 2-mercaptobenzimidazole in masterbatches is a completely satisfactory analytical method.

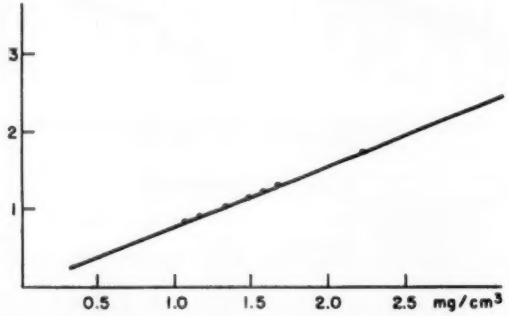


FIG. 11.—Calibration curve for determination of 2-mercaptobenzimidazole. Abscissa: concentration in mg per ml; ordinate: wave height in cm at E 1:50.

TABLE VIII

DETERMINING THE LIMIT OF ERROR ACCORDING TO THE CALIBRATION CURVE IN FIGURE 11

Concentration of 2-mercapto-benzimidazole, mg/ml		Error, %
Theoretical	Observed	
0.910	0.905	−0.55
1.000	0.996	−0.4
1.200	1.201	+0.09
1.500	1.500	0.0
1.600	1.590	−0.63
1.800	1.793	−0.39
2.000	2.002	+0.1

TABLE IX

POLAROGRAPHIC DETERMINATION OF 2-MERCAPTOBENZIMIDAZOLE IN MASTERBATCHES

Weight (g) of sample, master-batch	2-Mercaptobenzimidazole				
	Theoretical amounts, mg		Observed amounts, mg		
	per ml, in sample	in test solution	per ml, in test solution	in sample	Error, %
5.5027	500.2	1.429	1.425	498.75	−0.3
3.0055	500.91	1.431	1.424	498.4	−0.51

DETERMINATION OF MBT IN VULCANIZATES

A cured stock (see recipe No. 5) was extracted with methanol for 16 hours and then the extract was polarographed as previously described for MBT. The results disclosed that in comparison with MBT, the half wave potential was displaced to a lower value and that the typical steps did not appear in the c. v. curve for MBT. Neither do these steps appear upon polarographing the methanolic extract of an uncured stock (see recipe No. 6).

Recipe:	No. 5	No. 6
Crepe rubber	100	100
Zinc oxide	5	5
MBT	3	3
Sulfur	3	—

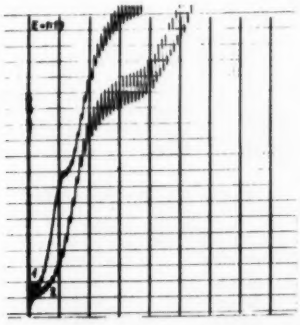


FIG. 12.—Polarograms of MBT, pure vs. extract. Curve *1*—MBT. Curve *2*—Extract of recipe 5.

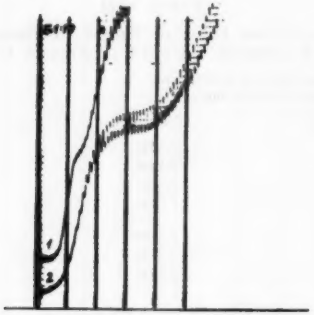


FIG. 13.—Polarograms of MBT, pure vs. extract. Curve *1*—MBT. Curve *2*—Extract of recipe 6.

The c. v. curves of both extracts are compared in the polarograms of Figures 12 and 13 with the c. v. curves of MBT dissolved in pure methanol. It seemed obvious to heat mixtures of MBT and zinc oxide in methanol under reflux for several hours and subsequently to examine the filtrate polarographically.

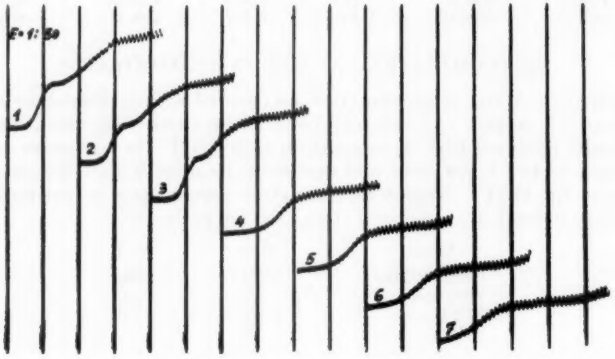


Fig. 14.—Current-voltage curves from the solutions or filtrates of Table X.

TABLE X (for Figure 14)

Curve	1	2	3	4	5	6	7
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zinc oxide	—	0.1	—	0.5	0.1	5.0	10.0
Methanol	100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE XI (for Figure 14)

	Amount (mg) of MBT		
Curve	Theoretical	Observed	Error, %
1	500.0	499.0	−0.2
2	500.0	394.0	−21.2
3	500.0	498.0	−0.4
4–7	500.0	0.0	−100.0

TABLE XII (for Figure 15)

Compound	MP13	MP14	MP15	MP16
Crepe rubber	100	100	100	100
Zinc oxide	20	20	20	20
MBT	10	15	20	25

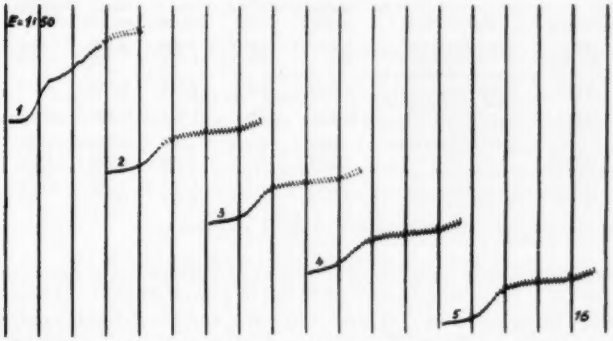


FIG. 15.—Polarograms of pure MBT compared with MBT extracted from masterbatches. Curve *1*—MBT. Curve *2*—Extract of MP 13. Curve *3*—Extract of MP 14. Curve *4*—Extract of MP 15. Curve *5*—Extract of MP 16.

Figure 14 reproduces a series of polarograms showing the influence of varying amounts of zinc oxide (Table X) on the wave height, the discharge potential, and the form of the c. v. curve for MBT. The data from this investigation make up Table XI.

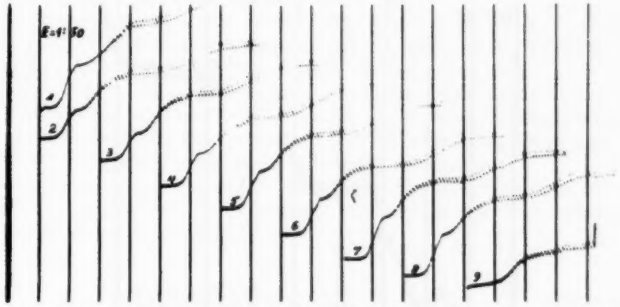


FIG. 16.—Polarograms of samples tabulated in Table XIV (see Table XIV). Curve *1*—MBT in methanol. Curve *2*—Acidified zinc salt of MBT. Curve *3*—MBT from MP 1 (after acetic acid treatment). Curve *4*—MBT from MP 6 (in methanol). Curve *5*—MBT from MP 7 (after acetic acid treatment). Curve *6*—MBT from MP 10 (in methanol). Curve *7*—MBT from MP 11 (in methanol). Curve *8*—MBT from MP 12 (in methanol). Curve *9*—Methanol extract of MP 7.

TABLE XIII (for Figure 16)

Compound	MP1	MP6	MP7	MP10	MP11	MP12
Crepe rubber	100	100	100	100	100	100
MBT	10	5	10	10	10	10
Zinc oxide	5	—	11	2	—	—
Magnesium oxide	—	—	—	—	2	—
Zinc stearate	—	—	—	—	—	2
Sulfur	—	5	5	5	5	5

TABLE XIV

DATA FOR POLAROGRAMS IN FIGURE 16

				MBT				
				Theory		Observed		
Curve	Sample	Test method	Weight sample	In sample, mg	In soln., mg/ml	In soln., mg/ml	In sample, mg	Error, %
1	MBT	in methanol soln.	0.5 g	500.0	1.428	1.425	498.7	−0.26
2	Zn salt	in methanol soln. after acidification	0.5	394.0	1.125	1.120	392.0	−0.50
3	MP1*	in methanol soln. after acidification	5.9998	259.6	0.741	0.740	259.0	−0.23
4	MP6*	in methanol ext.	11.004	500.1	1.428	1.425	499.1	−0.2
5	MP7*	in methanol soln. after acidification	6.0026	476.3	1.360	1.358	475.3	−0.2
6	MP10*	in methanol ext.	5.5203	471.8	1.348	1.200	420.0	−12.3
7	MP11*	in methanol ext.	5.5198	471.7	1.347	1.350	472.5	+0.1
8	MP12*	in methanol ext.	5.5366	473.1	1.351	1.350	472.5	−0.1
9	MP7*	in methanol ext.	5.4558	433.0	1.237	0.0	0.0	−100.0

* MP1: Uncured stock MP6, MP7, and MP10–MP12: Cured stocks.

Naturally the next question dealt with the influence of a fixed amount of zinc oxide on a variable quantity of MBT in a masterbatch. Therefore, the compounds listed in Table XII were extracted and the extracts analyzed with the polarograph (see Figure 15). The evaluation of these c. v. curves leads to the conclusion that the wave heights do not have a direct correlation with the MBT content. An additional example of the influence of zinc oxide on the wave height of MBT is also shown in Figure 16, Curve *6*. As long as zinc oxide, with respect to MBT, is not present in excess in the vulcanizate (see MP10, Table XIII) the characteristic c. v. curve of MBT appears upon examining the

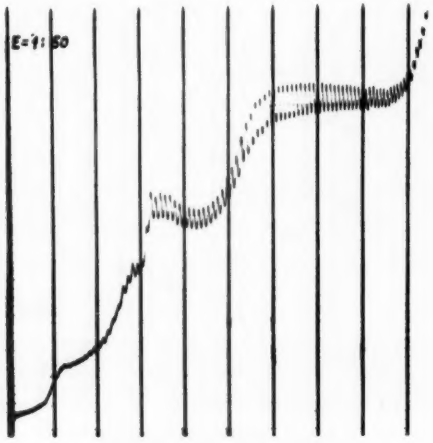


FIG. 17.—Determination of MBT in vulcanizate of MP 13.

TABLE XV (for Figure 17)

Weight of sample (MP 13), g	Amount of MBT		Error, %
	Calculated, mg	Observed, mg	
50.3796	312.4	297.5	−4.8

methanolic extract in the polarograph. However, here also the quantitative amount of MBT could not be ascertained from the wave height. The observed value was low by 12.3% (Table XIV).

Since the experiments repeatedly showed that zinc oxide influenced the typical c. v. curves of MBT or was responsible for their absence, a test was made to see if removal of the zinc would cause the characteristic waves of MBT to reappear.

A sample of a stock (MP 1, Table XIII) was ground and boiled for 30 minutes with acetic acid, then subsequently masticated several times in a mortar with acetic acid. From the combined acetic acid extracts hydrogen sulfide precipitated the zinc as the sulfide which was filtered off. The filtrate was extracted with ether, and the ether evaporated; the residue was dissolved in methanol and diluted to 100 ml in a volumetric flask. Polarographic analysis of this methanol solution produced the c. v. curve and half-wave potential typical of MBT. Evaluation of the wave heights gave satisfactory quantitative results (Table XIV). Curve *3* (Figure 16) illustrates the c. v. curve.

In order to test the ultimate effect of sulfur on the quantitative determination of MBT, the methanolic extract of the cured stock, MP 6, was examined polarographically. The experiment revealed that the sulfur present in the vulcanizate had no effect on either the trend of the curve or on the quantitative evaluation of the MBT wave (Figure 16, Curve *4*; Table XIV).

Handled similarly to MP 1 was cured stock MP 7. Here, too, the characteristic c. v. curve of MBT could be detected (Figure 16, Curve *5*). By way of comparison, Curve *9* shows again the deviating c. v. curve obtained from the unacidified methanolic extract.

Noteworthy is the fact that MBT could by crystallized out of the previously mentioned ether extract. The substance was purified by recrystallization and identified by melting point and mixed melting point.

Upon substituting magnesium oxide or zinc stearate for zinc oxide in MP 11 and MP 12, MBT may be quantitatively determined directly from the methanolic extracts of these vulcanizates (Figure 16, Curves *7* and *8*).

Table XIV lists the findings from the evaluation of the c. v. curves shown in Figure 16 and compares them with the theoretical values. The comparison reveals that polarographic determination of MBT in both uncured and cured stocks delivers completely satisfactory quantitative results.

However, in order also to test the usefulness of the polarographic determination of MBT in complex stocks, a quantitative determination was performed on the vulcanizate based on recipe MP 13.

MP 13

Crepe rubber	59.560
Naftolen ZD	2.080
Zinc oxide	12.100
Carbon black "elastic"	18.000
Carbon black "CK4"	2.400
Stearic acid	1.750
Ozokerite	0.830
PBNA	0.875
Sulfur	1.785
MBT	0.620
	100.000

The preparation of the sample was the same as described at the outset. The polarogram in Figure 17 illustrates the observed c. v. curve and Table XV

compares the theoretical with the observed value. In relation to the low concentration of MBT in the stock, the error of -5% may be regarded as completely practicable.

This paper does not deal with the other well defined waves noticeable in the above polarograms. A discussion of them is reserved for a later study.

SUMMARY

The present paper shows that the polarographic method for the determination of rubber additives (rubber chemicals) delivers fully usable results. The following points are discussed:

1. The method is qualified for a rapid quantitative determination of MBT and 2-mercaptobenzimidazole in raw materials control.
2. The zinc salt of MBT can be indirectly determined after its decomposition with acid.
3. MBT and 2-mercaptobenzimidazole can be determined directly in the methanolic extracts of masterbatches.
4. As with the masterbatches, MBT can be determined directly in the extracts of rubber stocks and vulcanizates when zinc oxide is absent. Magnesium oxide or zinc stearate do not interfere.
5. Experimental conditions are given which permit quantitative determinations of MBT in the presence of zinc oxide in uncured and cured rubber compounds.
6. The experiments have shown that the method is applicable to complex recipes containing MBT as the only accelerator. Of course, the limit of error is higher, that is, around -5%.

The investigations are being continued and the results will be presented at a later date.

ACKNOWLEDGMENT

The author wishes to thank Miss Zelder for carefully performing the numerous analyses.

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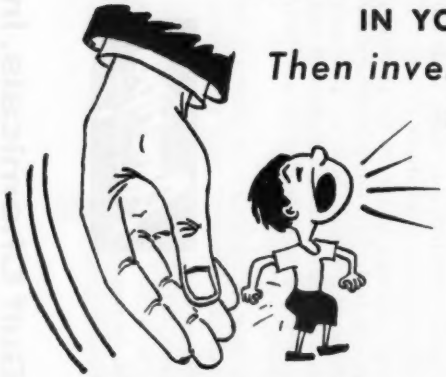

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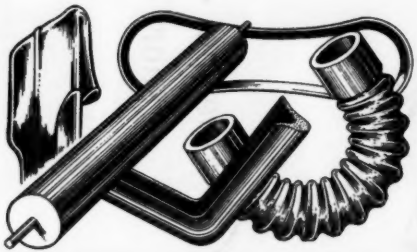

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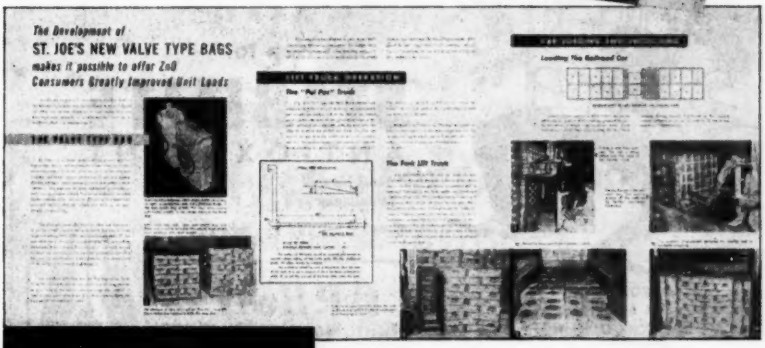

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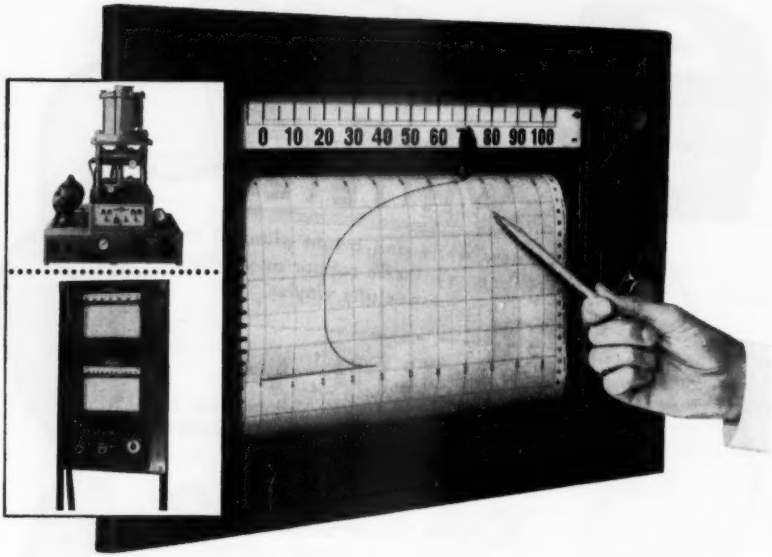

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